GeoRS

Geopedology and Landscape Development
Research Series

VOLUME 07

Anaerobic treatment of municipal organic waste from separate collection: digestate properties and substance flows during two-stage digestion and subsequent aerobic treatment

Christine Knoop

Brandenburg
University of Technology
Cottbus - Senftenberg

This series is edited by
Prof. Dr. Thomas Raab

Brandenburg University of Technology Cottbus - Senftenberg
Siemens-Halske-Ring 8
03046 Cottbus
Germany

ISSN 2196 -4122

DOI https://doi.org/10.26127/BTUOpen-4820
www.b-tu.de/fg-geopedologie/

Geopedology and Landscape Development
Research Series
GeoRS
Volume 7

Anaerobic treatment of municipal organic waste from separate collection: digestate properties and substance flows during two-stage digestion and subsequent aerobic treatment

Von der Fakultät für Umwelt und Naturwissenschaften der Brandenburgischen Technischen Universität Cottbus - Senftenberg zur Erlangung des akademischen Grades eines Doktor-Ingenieurs genehmigte Dissertation

vorgelegt von M.Sc. Christine Knoop aus Strausberg

Gutachter: Prof. Dr. phil. Thomas Raab

Gutachterin: Prof. Dr.-Ing. habil. Christina Dornack

Tag der mündlichen Prüfung: 03.07.2018

Summary

The provision of nutrients and organic matter to arable soils is critical to facilitate an intensive agriculture and secure long-term soil functionality. Municipal organic waste (MOW) is rich in nutrients and organic matter and its recycling onto agricultural lands presents a promising alternative to conventional fertilizers. In comparison to common aerobic treatment, the application of the biogas technology enables the recovery of both energy and soil amendments.

The introduction of a mandatory separate collection in Germany in 2015 reflects the political will to increase MOW recovery rates and facilitates its utilization as feedstock in biogas plants. However, MOW is a challenging feedstock as its composition varies and it is often contaminated with impurities such as plastics and metals. The two-stage anaerobic digestion process with dry fermentation is very robust and offers possibilities for process control so that no extensive MOW pretreatment is required. To close nutrient circles, remaining digestates shall be processed to soil amendments, which can be redistributed to arable land. However, less is known about digestate properties from two-stage digestion of MOW and how they are influenced during the treatment process. Furthermore, only scarce information on nutrient recovery rates and the accumulation of elements during processing is available. Therefore, this thesis investigates the development of digestate properties during anaerobic and subsequent aerobic treatment at laboratory and semi-industrial scale.

During a first experiment, changes in nutrient and heavy metal concentration in the solid digestate were monitored during anaerobic treatment of MOW in a two-stage laboratory biogas plant. A second investigation related amendment properties of MOW digestate of one origin to different post-treatment procedures. The impact of drying, composting and sieving on final digestate properties and specifically nutrient availability and heavy metal and carbon elution was evaluated. A third experimental approach investigated total material and substance flows during treatment of source-separated MOW in a semi-

industrial scale two-stage biogas plant and subsequent digestate composting including impurities removal.

Results show that MOW composition is rather heterogenic, which is reflected by a high variance of biogas yields and degradability as well as digestate properties. The heterogeneity of nutrient composition is much lower than the heterogeneity of heavy metal contents. A positive correlation was found between impurity contents and the concentration of Cd, Pb and Zn in the samples. The impurity content of investigated MOW samples is up to 12%. A few of the investigates MOW samples already exceed thresholds of BioAbfV for Cd, Pb and Zn. Results underline the influence of feedstock quality on final digestate characteristics. Organic matter degradation during biological treatment leads to further accumulation of unwanted substances. Subsequently, high impurities contamination of feedstocks and heavy metal redistribution during digestion and post-treatment become an exclusion criteria for soil amendments. Therefore, a low feedstock contamination needs to be striven to guarantee the production of marketable, high quality MOW-based soil amendments.

Results from the laboratory experiments show that nutrient and heavy metal concentration in the solid digestate is increasing during digestion except for N, P and Mg. The deficit of N, P and Mg amounts to the same extent of up to 45% and a struvite precipitation can be expected. There was also a deficit of Ca, Cd, Cr Ni, Pb and Zn in the solid digestate. This emphasizes that element retention in the digester system has a decisive impact on nutrient contents of digestates. Regular percolation transports mineralized elements from the location of release into storage tanks and the fixed-bed digester, where they may deposit. This distinguishes element distribution in two-stage systems from one-stage systems. In contrast, K is the only investigated element, which was completely rediscovered in the solid digestate during laboratory experiments. K^+ is assumed to adsorb to free exchange sites of existing molecular structures of the solid matter of digestate.

The total element mineralization was lower during semi-technical scale digestion, caused by shorter retention of MOW, which also resulted in a lower VS (volatile solids) degradation. Release of Mg did not occur to the same extent as for N and P. Consequently, as Mg is the limiting element for struvite precipitation, this effect is assumed to be rather low during semi-technical scale experiments. Furthermore, no K enrichment in the solid digestate was discovered during semi-technical scale experiments. Therefore, it can be concluded that K adsorption occurs only at longer retention times, which determines the rate of degradation, the complexity of the structure of the remaining organic matter and the number of free exchange sites. In comparison to nutrients, total heavy metal loads in the substrate flow were not significantly affected by semi-technical scale treatment. Therefore, the overall share of heavy metals in MOW is assumed to be present in stable compounds. However, results of laboratory digestion with longer retention time revealed a potential heavy metal release from MOW of up to 15% for Cd, Cr, Pb and Zn. The mobility of heavy metals may be promoted by dissolved organic carbon (DOC). When applicated to soil, organometallic complexes can easily be taken up by plants. Consequently, the binding of heavy metals onto soluble organic matter during digestion may lead to an increased heavy metal toxicity in soil after digestate application. To prevent this, impurities need to be removed from MOW in advance of anaerobic treatment.

Investigations on different treatment procedures confirm that in comparison to drying, composting of MOW digestates leads to a significant accumulation of K, P, Mg, Ca, Cd and Cr in the digestate. Although the element concentration is higher in composted batches, the water-extractability of nutrients, heavy metals and carbon is significantly lower than from dried batched. A significant correlation was found between the release of Zn, Ni, Ca, Mg and the pH as well as the DOC content of eluates. Results confirm that organic matter stability is a key factor regarding the potential performance of digestates in soil. The elution of DOC may be a good measure to evaluate digestate quality and to decide on treatment measures. Investigated digestates were characterized by a high residual degradation potential. Subsequently, for these digestates composting seems to be

the better treatment option as it leads to an improved organic matter stability and higher nutrient concentrations. However, heavy metal accumulation is problematic. Sieving of composted digestates showed that heavy metals are not evenly distributed and that highest heavy metal concentration can be found in the fractions below 1 mm. Consequently, sieving leads to further heavy metal enrichment in the digestate, as fractions with lower contamination are refused in the sieve overflow. Experiments also show that sieving below 10 mm is needed to ensure the legal threshold of 0.5% impurity content. However, this is related to a mass loss of up to 50%. Again, this emphasizes the importance of feedstock purity.

Investigations of semi-industrial scale MOW treatment show that about 60% of nutrients contained in the MOW inflow can be retained in the process outflow during two-stage digestion and subsequent aerobic post-treatment. A higher nutrient release was observed during digestion forced by percolation. Additionally, impurities removal causes a significant reduction of the final nutrient outflow. Based on the results of substance flow analysis, soil amendments from two-stage digestion and subsequent composting of 9 million tons of MOW could provide 1.5% of annual demand for N, 4.1% of annual demand for P and 3.3% of annual demand for K to agriculture. However, investigations have shown that N availability is very low in composted digestates. Consequently, the final output of investigated MOW treatment is most suitable to complement P and K fertilization.

Future research is needed to investigate the recovery of nutrients, which are mineralized during anaerobic treatment. Furthermore, the extent of heavy metal mobilisation remains unclear. A deeper understanding of how contaminants behave during biological treatment is needed to estimate the ecotoxicological potential of digestates when applied as soil amendments.

Zusammenfassung

Anaerobe Behandlung von Bioabfällen aus der getrennten Sammlung: Gärresteigenschaften und Stoffströme während der zweistufigen Vergärung und anschließenden aeroben Aufbereitung

Für eine intensive landwirtschaftliche Nutzung und die Sicherung der Fruchtbarkeit unserer Böden ist deren Versorgung mit Nährstoffen und organischer Substanz unerlässlich. Die Rückführung von Substraten auf der Basis von Bioabfällen aus der getrennten Sammlung in den natürlichen Stoffkreislauf kann eine Alternative zu herkömmlichen Dünge- oder Bodenhilfsmitteln sein. Neben der aeroben Kompostierung bietet sich der Einsatz der Bioabfälle in Biogasanlagen an, welcher neben dem stofflichen auch ein energetisches Recycling ermöglicht.

Die Einführung der flächendeckenden Getrenntsammlung von Bioabfällen im Januar 2015 in Deutschland soll die Nutzung dieser Ressource intensivieren und somit auch dessen Einsatz in Biogasanlagen steigern. Bioabfall ist aufgrund seiner schwankenden Zusammensetzung ein anspruchsvoller Einsatzstoff, der zusätzlich mit Störstoffen kontaminiert sein kann. Das zweistufige Biogasverfahren mit einer Trockenfermentation in der ersten Prozessstufe ist unempfindlich gegenüber Störstoffen und ermöglicht die Verwertung von Bioabfällen ohne aufwändige Vorbehandlung. Die am Prozessende verbleibenden Gärreste sollen aufbereitet und als Bodenverbesserer eingesetzt werden. Die dafür notwendigen Qualitätsanforderungen sind in der Bioabfallverordnung (BioAbV) und der Düngeverordnung (DüV) festgelegt. Wenig ist bekannt über Gärresteigenschaften aus der zweistufigen Bioabfallvergärung und wie diese durch die Prozessführung und anschließende Aufbereitung beeinflusst werden. Außerdem fehlen Informationen zu Nährstoffrückgewinnungsraten und der Anreicherung von Schwermetallen während des Behandlungsprozesses. Diese Dissertation befasst sich daher mit

der Entwicklung der Substrateigenschaften während der zweistufigen Vergärung und Aufbereitung von Bioabfällen im Labor- und Technikumsmaßstab.

Die Dissertation beschreibt und bewertet die Ergebnisse einer Versuchsreihe, welche die Veränderung der Gärresteigenschaften sowie die Anreicherung von Nährstoffen und Schwermetallen in Abhängigkeit von der Verweilzeit des Substrates in der zweistufigen Biogasanlage im Labormaßstab untersucht. In einer weiteren Versuchsreihe wurde die Entwicklung der Gärresteigenschaften während der Aufbereitung durch Trocknung oder Kompostierung sowie Fraktionierung betrachtet. Hierbei stand insbesondere die Verfügbarkeit und Freisetzung von Nährstoffen, Schwermetallen und Kohlenstoff im Fokus. Abschließend erfolgte die Untersuchung der Substrateigenschaften während der gesamten biologischen Behandlung der Bioabfälle im großtechnischen Maßstab und die Bilanzierung der Masse- und Stoffströme.

Acknowledgements

This thesis would have never been finished without the support of my supervisors, colleagues, friends and family.

I would like to thank Prof. Dr. Thomas Raab for supervision and support of my work on this thesis, especially for the motivating discussions, advice and encouragement during the preparation of manuscripts and the review process. I would also like to thank Prof. Dr. Christina Dornack for supervision and appreciation of my work and for encouraging me to do a doctoral thesis.

I deeply thank my colleagues for supporting me, for the cooperative atmosphere and for all the talk and laughter we had during our work. I especially thank Martina Heinrich for helping me with all the experimental and laboratory work and for being a reliable co-worker. Furthermore, I would like to thank Nils Dietrich for his commitment and ideas for the successful implementation of the research project VeNGA. I would also like to thank Michael Tietze for his support and advice during the investigations of the semi-industrial scale biogas plant and digestate composting. My thanks also go to the colleagues in the laboratory and all students that have been involved in the work of this thesis.

I would like to thank my friends and family for open ears and strong shoulders, for believing in me and encouraging me to keep up during less optimistic phases of my dissertation. I especially would like to thank my mum Dr. Sabine Knoop, who also supported me with linguistic assistance. I would also like to thank Ronny Tschirner for his optimism and encouragement during the last months.

The work of this thesis was part of the research project VeNGA (FKZ: 03EK3527) and I would like to thank the German Ministry of Education and Research (Bundesministerium für Bildung und Forschung – BMBF) for funding.

Table of contents

List of abbreviations and symbols

AAS	Atomic absorption spectroscopy
acc	Accumulated
BioAbfV	Bioabfallverordnung (German Biowaste Ordinance)
BGK	Bundesgütegemeinschaft Kompost (German Federal Compost Association)
BImschG	Bundesimmissionsschutzgesetz (German Law on Immission Control)
BMBF	Bundesministerium für Bildung und Forschung (German Federal Ministry for Education and Research)
BTU	Brandenburgische Technische Universität Cottbus-Senftenberg
c	Concentration
C	Carbon
C_{org}	Organic carbon
Ca	Calcium
Cd	Cadmium
CEC	Cation exchange capacity
CH_4	Methane
CHP	Combined Heat and Power
COD	Chemical oxygen demand
comp	Composted
Cr	Chromium
Cu	Copper
D	Digestate
D_{comp}	Composted digestate
D_{air}	Air-dried digestate
D_{oven}	Oven-dried digestate
dig	Digested
DM	Dry matter

DOC	Dissolved organic carbon
DU	Data uncertainty
DüG	Düngegesetz (German Fertilizing Law)
DüMV	Düngemittelverordnung (German Fertilizer Ordinance)
DüV	Düngeverordnung (German Fertilizing Ordinance)
E_{acc}	Element accumulation
EC	European Commission
EEG	Erneuerbare-Energien-Gesetz (German Renewable Energies Law)
F_{100}	Element retention of 100%
feed	Feedstock
FM	Fresh matter
FKZ	Förderkennzeichen
GICON	Grossmann Ingenieur Consult
IASP	Institut für Agrar- und Stadtökologische Projekte
ICP-OES	Inductively coupled plasma optical emission spectroscopy
in	Process input
K	Potassium
KrWG	Kreislaufwirtschaftsgesetz (German Closed Substance Cycle and Waste Management Act)
kWh	Kilowatt hour
LAGA	Länderarbeitsgemeinschaft Abfall (German Federal Working Group on Waste)
Mg	Magnesium
MF	Material flow
MFA	Material flow analysis
MOW	Municipal organic waste
MP	Methane potential
MP_{rem}	Remaining methane potential
MW	Megawatt
N	Nitrogen

Ni	Nickel
Nl	Norm liters
out	Process output
P	Phosphorus
pa	Plant available
Pb	Lead
PSU	Practical salinity units
S	Sulphur
SD	Standard deviation
SF	Substance flow
SFA	Substance flow analysis
TC	Transfer coefficient
VDI	Verein deutscher Ingenieure (German Association of Engineers)
VOA	Volatile organic acids
VS	Volatile solids
Zn	Zinc

List of figures

List of tables

List of equations

1 Introduction

The era of fossil resources is coming to an end. Our energy system is undergoing a turnaround which aims at a stronger utilization of renewable resources. Much research has been undertaken to develop and promote concepts for an alternative and sustainable way of energy production. One of these concepts is the production of biogas from organic substrates, which experienced a boom during the last 20 years. With more than 8000 biogas plants in operation today, Germany holds 31% of the world's biogas production capacity (IRENA, 2017). The success story began in the year 2000, when the German Renewable Energy Law (Erneuerbare Energien Gesetz, EEG) was implemented. It guaranteed the purchase of energy produced from biogas on the electricity market. The EEG amendment in 2004 introduced an additional bonus for the utilization of energy crops and led to an increase in maize cultivation and an investment wave in the biogas sector. However, in the following years the food or fuel debate and intensified land use brought about concerns about the carrying capacity of the existing biogas concept. With scarcity of fresh plant biomass on the market, the need for a second generation of biogas substrates became obvious.

Organic waste from municipalities (also referred to as biowaste) can be an interesting alternative feedstock for biogas plants. Within the last years, a legislative basis was created, which clearly promotes the use of organic residues for biogas production. Since January 2015 every German household is obliged to collect organic waste separately (Closed Substance Cycle and Waste Management Act/Kreislaufwirtschaftsgesetz, KrWG). With that, Germany implements the requirements of enhanced organic waste utilization from the Waste Framework Directive of the European Commission (2008/98/EC). The EC defines biowaste as all biodegradable garden and park waste, food and kitchen waste from households, restaurants and caterers and residues from the food processing industries. With the amendment of the EEG in 2012 the anaerobic

digestion of organic household waste became eligible. Under the amendment of the EEG in 2014 bonuses for energy crops digestion were cut completely, which further incited organic waste utilization in biogas plants. Today, about 100 biogas plants feeding municipal organic waste (MOW) are in operation. An increase is expected.

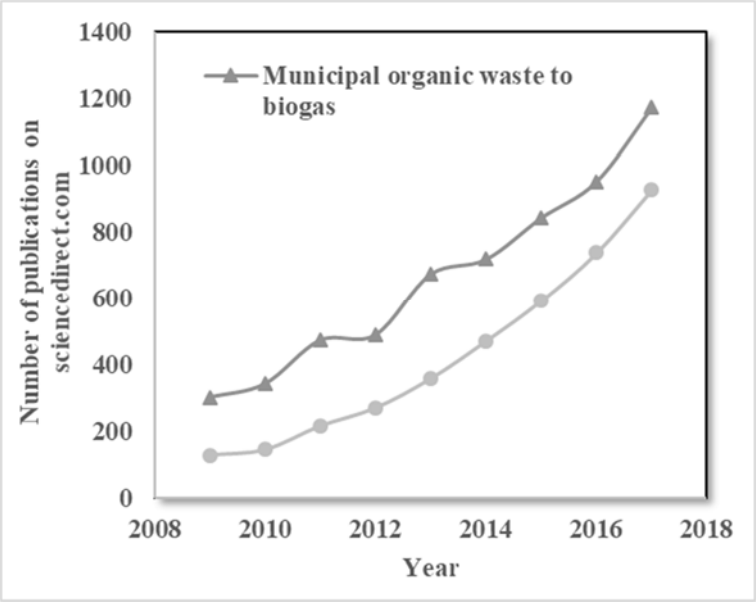

Figure 1: Number of publications on sciencedirect.com on the topics "digestate" and "MOW to biogas" during the last 10 years

The utilization of MOW in biogas plants results in a certain amount of digestion residues that are rich in organic matter and plant nutrients (Alburquerque et al., 2012b). This makes them a promising alternative to traditional organic fertilizers. There clearly is a need for the recycling of organic residues onto soil. The global demand for fertilizer will rise continuously. Nutrient scarcity can be foreseen especially for phosphorus (Drosg et al., 2015). Besides nutrients, the balancing of carbon in the soil is an important factor with regard to humus development and climate change mitigation. The recycling of MOW-based amendments onto

arable land enables replacing of nutrients and organic matter that may be depleted under intense cultivation (Odlare et al., 2011). It thereby makes an important contribution to maintaining and improving long-term soil fertility (Nkoa, 2014). Subsequently, the interest in digestate treatment and application is growing, which is reflected by the exponentially increasing number of publications on "digestates" and "MOW to biogas" throughout the last years (Figure 1). Still, there is a lack of knowledge with regard to fertilizing properties of MOW digestates and the influence of treatment on nutrient recovery potentials, which is addresses by this thesis.

2 State of research on municipal organic waste treatment and digestate utilization

2.1 Legal frameworks for MOW treatment and utilization

About 50 years ago, when waste generation started to increase severely in Germany due to economic growth and intensified consumption of goods, concepts and first legal frameworks for a modern and targeted waste management were developed (Bilitewski and Härdtle, 2013). Over time, the objectives of waste management in Germany have evolved from waste disposal on dumping sites to complex waste recycling and resource recovery. Accordingly, the legal requirements for waste treatment changed. The most relevant international and national regulations on the collection, treatment and recycling of municipal organic waste are summarized in Table 1.

The European Waste Framework Directive (2008/98/EC) provides general targets for waste management. In Article 1 (4) the following definition of bio-waste is given: "Biowaste means biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises and comparable waste from food processing plants". Furthermore, Article 22 of the European Waste Framework Directive addresses member states to encourage the separate collection and management of biowaste with regard to aerobic and anaerobic treatment and to utilize "materials produced from biowaste". With this, the incorporation of requirements on MOW recycling and end-of-waste criteria into national law was clearly emphasized.

Table 1: International and national regulations relevant for MOW treatment and amendment application

	Regulation	Came into force/ last amendment
International	**European Waste Framework Directive 2008/98/EC (Europäische Abfallrahmenrichtlinie)**	**2008**
National	**Closed Substance Cycle and Waste Management Act (Kreislaufwirtschaftsgesetz, KrWG)**	**2012/2017**
	Biowaste Ordinance (Bioabfallverordnung, BioAbfV)	**1998/2013**
	Fertilizing Law (Düngegesetz, DüG)	**2009/2017**
	Fertilizing Ordinance (Düngeverordnung, DüV)	**2017**
	German Fertilizer Ordinance (Düngemittelverordnung, DüMV)	**2012/2017**
	Law on Immission Control (Bundesimmissionsschutzgesetz, BImschG)	**2013/2017**
	Law on Renewable Energies (Erneuerbare-Energien-Gesetz, EEG)	**2014/2017**

By introducing the Closed Substance Cycle and Waste Management Act (Kreislaufwirtschaftsgesetz, KrWG) in 2012, Germany implemented the incentives given by the European Commission. In §3(7), it defines the term „Bioabfall" (biowaste), which resembles the one in the European Waste Framework Directive. Bio-waste refers to "all biological degradable material of

plant, animal or mushroom origin, which can be 1) garden and park waste, 2) landscape conservation waste, 3) food and kitchen waste from private households, restaurants, caterers, retail and food industry, 4) waste from others of similar properties". § 11(1) of KrWG obliges every German household to collect organic waste separately from January 2015. MOW shall be made available for a high-value recovery. Furthermore, the German federal government is empowered to define requirements for the collection, treatment, quality and utilization of MOW (§11(2)). The quality assurance of MOW and related products shall be monitored by authorized representatives (§12).

The quality requirements for MOW are regulated by the German Biowaste Ordinance (Bioabfallverordnung, BioAbfV). It was last amended in 2013. Again, the BioAbfV gives a definition of "Bioabfälle" (biowaste), which complements the definition in the KrWG by saying that biowaste is waste, "which can be degraded by microorganisms, soil biota or enzymes" (§2(1)). Furthermore, BioAbfV lists all specific waste materials the regulation refers to in the appendix. §2(2) defines the term "Hygienisierung" (hygienisation) and permissible treatment options for MOW. Referring to appendix 2, these are

- pasteurization (at 70°C for 1 hour, material homogeneity needs to be ensured, max. 12 mm particle size),
- composting (thermophilic temperature range (> 55°C for 2 weeks) and high biological activity based on ideal nutrient, aeration and moisture conditions (water content > 40%, pH 7) need to be ensured),
- thermophilic digestion (thermophilic temperature range (> 50°C) needs to be ensured during minimum residence time).

The temperature profile and treatment duration of the entire hygienisation process need to be monitored and documented. Additionally, treated MOW must be tested regularly to guarantee hygienic harmlessness and health safety as well as biological stability (§3, §3a). Heavy metal thresholds and quality requirements (pH, salt content, content of volatile solids, dry matter content, impurity content, stone content) as well as sampling methods and frequency are

referred to in §4. Depending upon heavy metal contents, total application quantities to arable land are restricted to 20 or 30 tons DM ha^{-1} in 3 years (§6). Furthermore, §9 requires an analysis of soil before the first application of MOW-based amendments. The BioAbfV is currently under review for a substantial reform. The future amendment will adapt to recent developments and will consider additional techniques of MOW treatment such as HTC processing or fuel generation (WEKA, 2015).

Besides the standards of BioAbfV, treated MOW that is supposed to be utilized as fertilizer or soil amendment also needs to comply with the legal requirements of German Fertilizing Law (Düngegesetz, DüG), German Fertilizing Ordinance (Düngeverordnung, DüV) and the German Fertilizer Ordinance (Düngemittelverordnung, DüMV). The DüG was amended in May 2017 to address the threat of increasing nitrate concentrations in the groundwater caused by nitrogen eutrophication. The release of the DüG amendment was especially expedited after November 2016, when the European Commission sued Germany for exceeding thresholds for nitrate (50 mg l-1) required by the European Nitrate Directive (91/676/EWG). The DüG defines the terms "Düngemittel" (fertilizer) and "Bodenhilfsstoff" (soil amendment) (§2). A fertilizer is "a material, that a) supplies nutrients to promote crop plant growth and increase plant yields and quality and b) maintains and promotes soil fertility". A soil amendment is "a material without significant nutrient content and microorganisms that is intended to a) impact on the biological, chemical and physical properties of soil to improve growth conditions for crop plants and b) promotes the symbiotic binding of nitrogen". Furthermore, DüG empowers the German government to release the DüV. The current DüV came into force in June 2017. It regulates the practical implementation of fertilization and defines related terms such as "Düngebedarf" (fertiliser requirement), "verfügbarer Stickstoff" (available nitrogen) and "Grundwasser" (groundwater) (§2). DüV stipulates application rates (§4) and accountable nutrients (§3), application times and blocking periods (§5, §6), fertilizer storage (§12) and application techniques (§11), incorporation (§6) and groundwater protection measures (§5). Furthermore, it requires a

documentation of the determination of fertilizer demands and a complete nutrient balance from every farm (§8, §10). The DüMV regulates the approval of fertilizers (§3), labelling of constituents (§6) and stipulates quality criteria with regard to hygiene (§5), nutrient contents and impurities (§4). Impurity criteria of recent DüMV are stricter than in the BioAbfV. Total impurity content (> 2 mm) must not exceed 0.5 % of DM, whereof only 0.1 % of DM can be plastic foils according to DüMV. With this, DüMV addresses the issue of MOW contamination by plastic bags.

As the quality, treatment and application of MOW are strictly regulated by the BioAbfV, DüV and DüMV with complex quality assessments for process outcomes, many treatment plants take part in voluntary certification by the Federal German Compost Association (Bundesgütegemeinschaft Kompost e.V., BGK). Specially trained personnel examine samplings of MOW-based products. After a one-year recognition procedure, treatment facilities undergo a regular monitoring including up to 12 samplings per year by the BGK. Samples are analyzed in certified laboratories. In this way amendment products can receive quality seals, which guarantee the compliance with legal quality requirements towards customers and consumers.
If MOW is treated in a biogas plant to recover methane, additional regulations need to be considered. The most important are the German Law on Immission Control (Bundesimmissionsschutzgesetz, BImschG) and the German Law on Renewable Energies (Erneuerbare-Energien-Gesetz, EEG). The BImschG addresses the prevention of harmful environmental impacts (§1, §5) and stipulates the approval for biogas facilities (§4). During the approval procedure, all potential environmental impacts of a facility need to be reviewed and evaluated (§6, §7). Thresholds for emissions and noise are defined by the technical guidelines TA Luft and TA Lärm. The extent of the procedure depends on the type of feedstock, size and capacity of the biogas plant.

The EEG shall ensure a sustainable energy supply based on renewable resources (§1). It defines expansion targets (§4), regulates electricity input (§11, §14), feed-

in-tariffs and bonus allocation (§20, §21, §50) and tendering procedures (§30a – §35a). It also regulates feed-in tariffs for energy generated from anaerobic treatment of MOW (§43). Under the recent EEG amendment from July 2017, biogas facilities with an input of more than 90% MOW (as defined by KrWG) and a plant capacity of up to 500 kW receive 14.88 cents kWh^{-1}. Facilities with up to 20 MW capacity get 13.05 cents kWh^{-1}. In comparison, feed-in-tariffs for energy from renewable biomass ranges from 5.71 cents kWh-1 to 13.32 cents kWh^{-1}. Higher feed-in-tariffs for electricity obtained from anaerobic treatment of MOW clearly underline the political turnaround towards an enhanced exploitation of organic waste for energy recovery.

To sum up, it can be said that plant operators for MOW treatment act within a broad and complex system of legal frameworks. Depending on current findings from research, practical experience, environmental responses and overall political incentives these regulations are subject to constant change. This could be seen in the debate on nitrate exposure of groundwater and the related adaptations of fertilizing requirements or also with regard to regular amendments of the EEG. These legislative changes require a high flexibility of plant operators. A recirculation of MOW onto arable land is only possible if the quality of amendments can be ensured. Citizens acting as waste producers as well as the municipalities in charge of waste disposal and waste treatment facilities need to be sensitized to prevent a contamination of MOW products with impurities and pollutants. Legal frameworks aim at quality assessment, which shall protect society from environmental threats and ensure the maintenance of the long-term functionality of the resources soil and water.

2.2 MOW quantities and recovery in Germany

The utilization and recirculation of MOW is a concept familiar to every gardener. The separate collection of MOW aims at providing a resource and has been in existence for more than 30 years (Fricke et al., 2013). However, there has never been a complete, nationwide capture of MOW. Latest statistics from 2014 (Destatis, 2017) confirm a total amount of separately collected MOW of 9.8 million tons, whereof 4.6 million tons were captured on-site in biowaste bins. 5.2 million tons were separately collected park and garden waste. Kern and Siepenkothen (2014) estimate that about 4.7 million tons of MOW are still disposed in bins for residual waste. One reasons for that is the low connection rate of households of only 52% in 2010 (Krause et al., 2014). Furthermore, up to 42% of produced MOW are treated by private composting (Krause et al., 2014). With the implementation of KrWG and the obligation for every household to carry out a separation of organic residues entrusted to waste treatment by 2015, total collection quantities of MOW shall be increased. Thereby, an essential milestone for the expansion of MOW recovery can be achieved. According to different studies the amount of MOW that may potentially be collected in biowaste bins on-site, is estimated to be between 7.5 million tons $year^{-1}$ (Kern and Raussen, 2014) and 9 million tons $year^{-1}$ (Fricke et al., 2013; Krause et al., 2014).

In Germany, MOW is commonly treated in about 1000 composting plants (Kern et al., 2012). Altogether, up to 90% of captured MOW is processed by aerobic treatment (Kern et al., 2012). Different composting procedures such as tunnel, container or heap composting are applied. The anaerobic treatment is less pronounced, but has gained importance during the last years of biogas boom in Germany. Reasons for the slower development of biogas technology for MOW treatment were technical and economic obstacles. In comparison to aerobic treatment facilities, biogas facilities for MOW require higher efforts with regard to process control and failure susceptibility as well as higher investment and operation costs (Fricke et al., 2013). However, technological advances,

adaptations of BImschG and subsidies from EEG have improved and aligned framework conditions for plant operators. In 2015 total digestion capacity for MOW was 1.9 million tons year^{-1} provided by over 100 biogas plants (Kern and Raussen, 2014). An expansion of anaerobic treatment facilities up to a capacity of 5.5 million tons year^{-1} is expected by 2025 (Kern and Raussen, 2014).

Treatment and process outputs highly rely on the composition and quality of MOW (Bilitewski and Härdtle, 2013; Kern et al., 2012), which is influenced by different factors (Campuzano and González-Martínez, 2016) such as:

- Season dependent fluctuations and cooking habits
- Bin size
- Collection frequency
- Territory structure of collection area (urban, rural)
- Waste fee system
- Public relations and integration of local communities

With regard to energy recovery via anaerobic digestion, the share of easily degradable organic matter is crucial. MOW rich in kitchen or food waste will achieve higher biogas yields (Fricke et al., 2013; Pavi et al., 2017). A few studies investigated methane yields from MOW as reviewed by Campuzano and González-Martínez (2016). Average methane yields range from 180 Nl kg^{-1} VS to 580 Nl kg^{-1} VS, indicating a high variance of results caused by composition fluctuations, which is also reflected by variabilities of results on chemical characteristics. Properties of MOW are investigated in section 6 (Table 13).
The recent state of knowledge and technologies as well as political incentives show that the recovery of the energetic potential of MOW can contribute to future energy supply and therefore shall be given priority over composting. However, relevant obstacles for the expansion of anaerobic treatment facilities exist such as tendering conditions for MOW treatment, low available annual MOW quantities, high efforts of approval procedures for plant adaptations and high coverage of composting plants (Scholwin et al., 2013). Still, practical examples of several municipalities show that the management of MOW can be

economically feasible if local businesses, administration and the public cooperate. Local master plans for high MOW capture, good MOW quality and a revenue-oriented treatment shall be developed on community level.

2.3 Sampling and analysis of MOW

Determining the characteristics of a MOW batch proceeds in the following steps: 1) planning of sampling, 2) sampling, 3) sample preparation and 4) sample analysis. MOW is a solid, heterogenic substrate (DM > 20%, coarse particle size of 50-120 mm), which is usually available as aggregate material (Figure 2).

Figure 2: Impressions from MOW sampling

Conscious sampling and sample preparation are an integral part of MOW analysis, which is crucial to ensure representative results. Different provisions exist, which define standards for sampling and pretreatment procedures, technical equipment, analysis methods and related documentation. For MOW, BioAbfV provides the legal baseline. Additionally, sampling and analysis standards required by BioAbfV are complemented by advanced instructions from different institutions. With regard to MOW treatment, most important additional provisions are the LAGA PN98 (2001) and the LAGA method collection 3.0 (2016) by the Federal Working Group on Waste (Länderarbeitsgemeinschaft, LAGA), the methods book (2014) of the German Federal Compost Association (Bundesgütegemeinschaft Kompost e.V., BGK)

and the guideline VDI 4630: Fermentation of organic materials: Characterization of the substrate, sampling, collection of material data, fermentation tests (2016) by the Association of German Engineers (Verein Deutscher Ingenieure, VDI). An overview of recommended methods for MOW sampling and analysis is presented in Table 2.

Appendix 3 of BioabfV stipulates the requirements for sampling and analysis of MOW. According to passage 1.1, sampling of solid, treated or non-treated MOW shall be examined as defined in DIN EN 12579 (Soil improvers and growing media - Sampling; German version). DIN EN 12579 requires at least 12 withdrawals from every MOW batch. The composite sample is homogenized and reduced by quartering until a quantity of 5 liters is reached in the final sample. Sampling needs to be documented. One final sample of each batch is subsequently treated and analyzed in the laboratory. LAGA PN98 describes sampling in more detail than DIN EN 12579 and recommends at least 8 withdrawals from 3 vertical sampling slots. Furthermore, the distribution of sampling points shall consider the conical shape of aggregate material, so that from the lower zone a higher share of MOW is sampled. After subsampling, two final samples of 5 liters each (10 liters in total) shall be provided for laboratory analysis. Methods book of BGK provides a detailed listing of suitable sampling equipment. Furthermore, it recommends at least 10 withdrawals of 3 liters from two sampling slots. After subsampling, a sample of 20 liters shall be provided for the laboratory analysis, whereof 5 liters will be used for dry matter investigations. VDI refers to standards of LAGA PN98.

Table 2: Overview of recommended methods for sampling and analysis of MOW (marks the method applied during laboratory analysis of this thesis)*

Analysis Parameter	Acronym	Method	Short discription	Reference
Sampling	-	DIN EN 12579	12 withdrawals, 1 laboratory sample per batch (5 liters)	BioAbfV
		LAGA PN98	8 withdrawals, 2 laboratory samples (5 liters)	LAGA
		BGK Methods book	10 withdrawals, 1 laboratory sample (20 liters)	BGK
		VDI 4030	refers to LAGA PN98	VDI
Sample preparation	-	DIN EN 13040	Sieving (40 mm, 25 mm), drying (75°C), crushing	BioAbfV
		DIN EN 13650	Grinding of dry sample (grain size 500 µm)	BioAbfV
		DIN 19747*	Drying (40°C), sieving (40 mm, 10 mm), shredding & homogenization, drying (105°C)	LAGA
		DIN EN 13567*	Grinding of dry sample (grain size 250 µm)	LAGA, BGK
Aqua regia digestion	-	DIN EN 13650	Digestion in return condenser	BioAbfV
		DIN EN 13567*	Pressure digestion in microwave	LAGA
Dry matter content	DM	DIN EN 13040*	Drying at 103 +/- 2°C, until weight constancy	BioAbfV, BGK
		DIN EN 14346	Drying at 105 +/- 3°C, until weight constancy, min 12 hours	LAGA
Volatile solids	VS	DIN EN 13039	Muffle furnace at 450°C	BioabfV, BGK
		DIN EN 12879*	Muffle furnace at 550°C	BGK
		DIN EN 15169	Muffle furnace at 550°C	LAGA
Impurities	-	BGK Method book*	Drying & sieving (10 mm, 2 mm) of 3 liters FM	BioAbfV, BGK
Total carbon/ Total organic carbon/ Dissolved organic carbon	TC/ TOC	DIN EN 13137	Incineration at 900°C	LAGA
		DIN EN 15936	Incineration at 900°C	LAGA
		DIN ISO 10694*	Incineration at 950°C	BGK
	TOC/DOC	DIN EN 1484	Oxidation, CO_2 quantification	LAGA
Methane potential	MP	DIN 38414-8	CH_4 development at 37°C for 21 days	LAGA
		VDI 4030*	CH_4 development at 37°C for 25 days	VDI
pH	pH	DIN EN 13037	H_2O-extraction 1:5	BioAbfV, BGK
		DIN EN 15933	$CaCl_2$-extraction 1:5	LAGA
		VDLUFA Methods book*	$CaCl_2$-extraction 1:10	BGK
Salinity	Sal	DIN EN 13038	H_2O-extraction 1:5	BioAbfV, LAGA, BGK
		VDLUFA Methods book*	H_2O-extraction 1:10	BGK
Nitrogen	N	DIN ISO 13878*	TNb, incineration at 900°C	LAGA
		VDLUFA Methods book	Kieldahl-N	LAGA, BGK
Ammonium	NH_4-N	DIN EN 14671	KCL-extraction	LAGA
		DIN EN ISO 11732	Flow injection analysis	LAGA
		DIN 38406-5	Photometric determination	BGK
		VDLUFA Methods book*	$CaCl_2$-extraction 1:10	BGK
Nutrients	P, K, Mg, Ca	DIN EN ISO 11885*	ICP-OES	LAGA
		DIN EN ISO 22036	ICP-OES	LAGA
Heavy metals	Cd, Cr, Cu, Ni, Pb, Zn	DIN EN ISO 11885*	ICP-OES	BioAbfV, LAGA
		DIN EN ISO 17294-2	ICP-MS	BioabfV, LAGA
		DIN EN ISO 22036	ICP-OES	LAGA
		DIN EN ISO 38406	Graphite-furnace AAS	BioAbfV
		DIN EN ISO 11047	Flame AAS	BioAbfV
		DIN EN ISO 5961	Graphite-furnace AAS	BioAbfV
		DIN EN 1233	Graphite-furnace AAS	BioAbfV

In the laboratory, the final sample undergoes pretreatment, which is usually a sequence of drying, sieving and grinding. Passage 1.2 of appendix 3 of BioAbfV thematises requirements of sample preparation of MOW. Samples shall be prepared according to DIN EN 13040 (Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density; German version) and DIN EN 13650 (Soil improvers and growing media - Extraction of aqua regia soluble elements; German version). According to DIN EN 13040 MOW shall be homogenized by sieving at 40 mm and 25 mm and subsequent shredding of sieve overflow. Afterwards, the sample is dried at 75 °C to enable further crushing. Finally, it is treated at 105 °C to measure the dry matter content. DIN EN 13650 requires grinding of the dry sample until a grain size of < 500 µm is reached. However, LAGA considers that DIN EN 13040 and DIN EN 13650 are obsolete with regard to current laboratory standards and recommends replacing them by DIN 19747 (Investigation of solids – Pre-treatment, preparation and processing of samples for chemical, biological and physical investigations) and DIN EN 13567 (Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements; German version). The proceedings of DIN 19747 show significant differences in sample treatment. First, MOW shall be dried at 40 °C. Subsequent sieving at 40 mm and 10 mm divides the sample into a fine (< 10 mm), middle (10-40 mm) and a coarse (> 40 mm) fraction, which can be subsampled and shredded. After mixing all fractions, a share of the sample is dried at 105 °C for 24 hours to determine the dry matter content. According to DIN EN 13567 the dry sample shall be grinded until a grain size of 250 µm is reached. The methods book of BGK also recommends sample (at least 100 g) comminution until 250 µm particle size. This ensures high sample homogenization and pulping. The pulping procedure of DIN EN 13567 stipulates pressure digestion with aqua regia in a microwave, which facilitates a complete dissolution of elements. With this, DIN EN 13567 represents the recent state of elemental analysis, which outdated the requirements of DIN EN 13650 (aqua regia digestion in a return condenser).

Appendix 3 passage 1.3 of BioAbfV defines parameters that shall be analyzed stating relevant methods. These parameters include dry matter content (DIN EN 13040), volatile solids (DIN EN 13039), stone & impurity content (methods book BGK), pH (DIN EN 13037), salinity (DIN EN 13038) and content of heavy metals (DIN 38406, DIN EN ISO 11885, DIN ISO 11047, DIN EN ISO 17294-2, DIN EN ISO 5961, DIN EN 1233, DIN EN 1483 or DIN EN 12338). In the LAGA method collection, the German Federal Working Group on Waste recommends a few adaptations of analysis methods according to recent laboratory standards. Especially, elemental analysis in the aqua regia extracts shall be examined with ICP-OES or ICP-MS according to DIN EN ISO 11885, DIN EN ISO 22036 or DIN EN ISO 17294-2. Determination of elements with atomic absorption spectroscopy (AAS) as required by BioAbfV according to DIN EN ISO 38406, DIN EN ISO 11047, DIN EN ISO 5961, DIN EN 1233 and DIN EN 12338 is outdated and shall be replaced. Furthermore, the LAGA methods collection defines reference methods for the analysis of all relevant waste parameters. The German Federal Compost Association (BGK) focusses on analysis methods for soil amendments and mainly refers to requirements of BioAbfV. Additionally, for the determination of pH, salinity and NH_4-N, methods of German Association of Agricultural Analysis and Research Institutions (Verband deutscher landwirtschaftlicher Untersuchungs- und Forschungsanstalten, VDLUFA) are recommended. This indicates the relevance of investigated organic amendments for the agricultural sector. Furthermore, BGK gives reference ranges and repeatability limits for composts.

The review of provisions for MOW sampling as well as sample pretreatment and analysis shows that there exists a wide and partly divergent range of demands and recommendations. Every sampling and analysis strategy depends on the characteristics of the investigated MOW batch. Heterogeneity, total volume and particle size determine sampling technique, number of single withdrawals, the volume of the laboratory sample, safety measures and sample packaging. However, some requirements of BioAbfV seem to be outdated with regard to recent laboratory procedures. Other parameters such as N/NH_4-N, P, K and C

content as well as methane potential (MP) are ignored by BioAbfV. Based on available methods and recommendations as well as laboratory equipment, sample handling the investigations of this thesis was set. A detailed description of sampling can be found in section 3.2. Furthermore, analysis methods used are explained in sections 4-6.

2.4 The anaerobic digestion process

Anaerobic digestion is a natural process where methane is produced due to organic matter degradation by microorganisms in an oxygen-free environment. Since the end of the 19th century, anaerobic digestion has been used for the treatment of wastewater (Rosenwinkel et al., 2015). The development of advanced and efficient digester systems lays the foundation for the utilization of organic waste in biogas plants (Bilitewski and Härdtle, 2013). Especially, MOW from separate collection, food waste from caterings and green waste are promising substrates for an energetic recovery by anaerobic treatment (Appels et al., 2011; Kern et al., 2012).

The anaerobic digestion follows a degradation reaction chain, which is comprised of four steps. First, during hydrolysis macromolecular organic matter consisting of carbohydrates, proteins and fats is broken down by microbial exoenzymes. Second, during acidogenesis the obligate and facultative anaerobic bacteria degrade solved products into short-chain organic acids, alcohols, H_2 and CO_2. Third, during acetogenesis reaction products from the second step are converted into acetic acid. Finally, during methanogenesis strongly obligate bacteria transform acetic acid, H_2 and CO_2 into methane (CH_4). The involved microorganisms have typal living requirements, which need to be kept within an optimal range during the anaerobic digestation process to ensure sufficient organic matter conversion in the biogas plant. Subsequently, process management influences the composition of the microbiological community in the anaerobic digester. Especially methanogenic bacteria are sensitive to process fluctuations (Ward et al., 2008). Important influence parameters are

temperature, pH, availability of nutrients and trace elements, substrate mixing, retention time and feedstock properties. Consequently, suboptimal process conditions lead to an inhibition of bacterial activity and reduced biogas yields (Chen et al., 2008). Plant setting strives to provide optimal conditions for anaerobic digestion. Depending on the temperature, different microbial communities develop. Commonly, anaerobic digestion runs at mesophilic (34-42 °C) or thermophilic (50-60 °C) temperature level (Fricke et al., 2014b; Khalid et al., 2011). The process performance, e.g. metabolic rates and bacteria growth rates, increases with rising temperatures. However, thermophilic processes are more sensitive to process fluctuations and usually require a higher energetic input (Kim et al., 2002). Microorganisms are also very sensitive to pH variations. Each process step of anaerobic digestion requires a different pH level. Fermentative bacteria favour a pH range from 4.0 to 8.5, while most methanogenic bacteria prefer a tight pH range from 6.5 to 7.2 (Chen et al., 2008; Khalid et al., 2011). The pH is influenced by the evolution of organic acids (mainly acetic acid, propionic acid, butyric acid, and valeric acid) during the first steps of anaerobic degradation. Subsequently, a strong pH decrease caused by accumulation of organic acids can inhibit the activity of methanogens. The individual buffer capacity of substrates counteracts pH drop. This means that temperature, pH and the total organic acid load in comparison to the buffer capacity are the parameters that need to be continuously monitored to evaluate the performance of the biogas process and to decide on short-term optimization measures.

There are different biogas procedures. The classification of procedures is done with regard to feedstock characteristics and supply as well as plant layout and process settings. Depending on the dry matter content of digester inflow, a distinction can be made between dry and wet fermentation with continuous or discontinuous feedstock supply. Moreover, plant layout can be single-stage or two-stage. Within this overall categorization, there are different types of anaerobic digesters. The reactor design has a strong effect on the process performance (Khalid et al., 2011; Teglia et al., 2011b). The choice of plant and

process settings depends on the regional availability and properties of feedstock as well as on the economic efficiency influenced by the local boundary conditions. Within the last decade a significant development of biogas technologies has been observed, which contributed to the expansion of anaerobic treatment facilities for MOW. Today, mainly dry fermentation plants are operating MOW in Germany as they have proved to be more impurity tolerant with regard to process wear (Fricke et al., 2014b). Discontinuous and continuous procedures are balanced. The application of the mesophilic temperature range prevails (Kern and Raussen, 2014).

Anaerobic digestion of organic waste from households was investigated by several authors (Braguglia et al., 2017; Khalid et al., 2011; Pavi et al., 2017; Zhang et al., 2014). In comparison to conventional feedstocks such as manure or energy crops, the anaerobic treatment of MOW is more elaborate. MOW contains a higher share of easily degradable organic matter and simple sugars (Campuzano and González-Martínez, 2016), which causes a very rapid acidification of feedstocks, and bears the risk of reactor overload and process deterioration (Chen et al., 2008; Khalid et al., 2011). Additionally, the composition of MOW feedstocks is heterogenic leading to strong variations in methane yields (Campuzano and González-Martínez, 2016; Pavi et al., 2017). Impurities resulting from miss-sorting can be another reason for process disturbances and devise failure. The separation and homogenization of feedstocks (Fricke et al., 2014a) and the utilization of digestates as inoculum (Khalid et al., 2011) are commonly applied measures to stabilize the digestion process. Furthermore, an intense process monitoring is required to ensure successful anaerobic treatment of MOW.

To sum up, it can be said that anaerobic digestion is a complex process, which heavily relies on the activity of microorganisms with specific living requirements. So far, research has mainly focused on the development of technologies and the controlling of the biogas process with regard to highest possible biogas yields. The fate of elements during anaerobic treatment was investigated by some

authors (Banks et al., 2011; Bauer et al., 2009; Massé et al., 2007; Möller and Müller, 2012; Schattauer et al., 2011; Zirkler et al., 2014) showing that composition and availability of nutrients change due to organic matter mineralization and biochemical transformation processes during digestion. Some authors investigated the transformation of organic matter during anaerobic treatment (Abdullahi et al., 2008; Tambone et al., 2009) and show that after digestion solid remains contain less accessible organic compounds of higher structural complexity. The release of nutrient elements and the formation of new compounds influence the distribution and retention of substances in the process (Möller and Müller, 2012). Furthermore, there is evidence that a loss of nutrient elements may occur during anaerobic treatment due to precipitations of salts such as metal sulfides or phosphates, which retain in the digester system (Banks et al., 2011; Zirkler et al., 2014). Finally, microorganisms utilize a certain amount of nutrients provided by the feedstock (Facchin et al., 2013; Khalid et al., 2011; Schattauer et al., 2011).

2.5 Digestate properties

After the anaerobic treatment process is completed, the digestate remains. It contains heavily degradable and non-degradable organic and anorganic matter as well as significant amounts of process liquid depending on the digestion system applied (Abdullahi et al., 2008; Tambone et al., 2010; Teglia et al., 2011a). So far, digestate recovery has been of minor interest and residues from anaerobic treatment of MOW have more or less been disposed by plant operators without economic benefits. However, within the last years, the utilization and marketing of digestates has become more interesting due to nutrient scarcity, carbon deficiencies of soil and strong overall incentives for nutrient and organic matter recycling (EU Directive 2008).

Properties of digestates were investigated by several studies (Bolzonella et al., 2017; Drosg et al., 2015; Kluge, 2008; Lorenz et al., 2014; Möller et al., 2010; Möller and Müller, 2012; Nkoa, 2014; Risberg et al., 2017; Tambone et al., 2017;

Tambone et al., 2015; Tambone et al., 2010; Teglia et al., 2011a; Zirkler et al., 2014). Various types of feedstocks and combinations have been reported. Consequently, the diversity of the biomass input reflects the variability in the composition and biochemical properties of digestates (Nkoa, 2014; Risberg et al., 2017; Teglia et al., 2011a; Zirkler et al., 2014). The liquid fraction of digestates is rich in solubilized nutrients especially N and K (Akhiar et al., 2017; Lorenz et al., 2014; Möller et al., 2010) and has a great potential to be directly applied as fertilizer (Nkoa, 2014). Due to the alkaline pH, liquid digestates are subject to N loss by ammonia volatilization (Lorenz et al., 2014; Möller et al., 2010). The solid fraction of digestates contains organic matter and organically bound nutrients and is preferentially used as soil amendment (Nkoa, 2014). However, research on digestates largely focuses on remains resulting from the anaerobic treatment of agricultural feedstocks such as manure, energy crops and agro-industrial products. Moreover, most studies focus on primary macronutrients (N, P, and K) and available data on other major nutrients and essential micronutrients including calcium (Ca), magnesium (Mg), sulfur (S), copper (Cu), iron (Fe) and zinc (Zn) is scarce.

Some authors investigate properties of digestates from MOW treatment (Govasmark et al., 2011; Kluge, 2008; Kupper et al., 2014; Lorenz et al., 2014; Massaccesi et al., 2013; Odlare et al., 2011; Saveyn and Eder, 2014; Tampio et al., 2016; Teglia et al., 2011a). 2.8 million tons of MOW digestates are produced by treatment facilities in Germany every year (Saveyn and Eder, 2014). Compared to conventional digestates or composts, data on MOW digestates are less abundant. This is presumably caused by the predominance of agricultural biogas plants and stricter legal requirements, which prohibit direct application of MOW digestates. Properties of digestate such as nutrient content, organic matter stability and contamination with heavy metals and impurities need to be known to estimate the ecological and the economic value of MOW digestates, to decide on post-treatment measures and to meet legal application requirements.

The results on nutrient contents of digestates from literature are diverse. Especially N, P and K show big variances. Similar results were found by reviews on digestate properties by Nkoa (2014) and Möller and Müller (2012). The nutrient content in the digestates is related to the nutrient content of feedstocks (Drosg et al., 2015; Risberg et al., 2017; Tampio et al., 2016). Consequently, the utilization of feedstocks with high N and P contents like pig slurries or cattle manure will increase nutrient contents of digestates (Bustamante et al., 2013; Drosg et al., 2015; Möller and Müller, 2012). Solid digestates contain significantly higher concentrations of P and organic N but a low share of available N (Lorenz et al., 2014; Möller et al., 2010; Odlare et al., 2011; Tampio et al., 2016).

Results from the literature review show, that MOW digestates can be contaminated with heavy metals and organic pollutants (Al Seadi et al., 2013; Govasmark et al., 2011; Kupper et al., 2014; Massaccesi et al., 2013; Saveyn and Eder, 2014). Especially impurities can be sources of contaminants (Smith, 2009). However, Kupper et al. (2014) found that heavy metal contents in digestates are mostly below legal thresholds and that contamination occurs at random, which causes a rather heterogenic distribution of heavy metals. Furthermore, most heavy metals in MOW are expected to be recalcitrant towards the aerobic and the anaerobic degradation process (Kupper et al., 2014) so that risk associated with chemical contamination of the food chain or the environment from agricultural use of MOW digestates seems low (Govasmark et al., 2011). However, organic matter degradation leads to an increase of relative heavy metal concentrations in the solid residue (Fricke et al., 2014a) and some digestates are reported to have high Cu and Zn contents (Bustamante et al., 2013; Saveyn and Eder, 2014). Furthermore, depending on the separation technique applied, heavy metal contents of liquid digestates can be higher due to the higher sorption of metals onto fine particles < 250 µm (Kupper et al., 2014).
The impurity content of digestates is a crucial quality criterion. However, it plays a minor role in the literature. Kluge et al. (2008) did not detect impurity contamination in agricultural digestates. And Saveyn and Eder (2014) state that MOW digestates derived from source-separated inputs tend to meet limit values

easily. However, Kehres (2016) points out that high impurity levels above 3% in the feedstock lead to significant quality losses in MOW-based products, due to low removal opportunities during treatment. Therefore, the impurity content of MOW digestates should be carefully monitored.

In summary, it can be said that MOW digestates contain a wide range of nutrients, which makes them an attractive product for nutrient and carbon recycling onto agricultural land. However, MOW digestates may also contain heavy metals, impurities and organic pollutants which can be a problem with regard to the legal quality requirement for digestates and related soil amendments. Consequently, feedstock composition and purity strongly predetermines the quality of treatment outputs.

2.6 Treatment and utilization of digestates

Most commonly, digestates are used as fertilizer or soil amendment to contribute to nutrient and carbon recovery (Drosg et al., 2015). Direct application without digestate processing is one important recycling path. However, untreated digestate contains a large amount of water (> 80%), which causes high specific transportation costs depending on the plants' location (Delzeit and Kellner, 2013) that exceed benefits from nutrient recycling. Further costs are related to investments in storage capacity as well as to handling and application of digestates (Drosg et al., 2015). Additionally, legal restrictions on nitrogen limits impede direct application of digestates. Moreover, digestates from MOW treatment need to meet the requirements for hygiene, stability and heavy metal thresholds of BioabfV. Consequently, digestate treatment becomes an inevitable part for operation of biogas plants (Dahlin et al., 2015).

Digestate processing can be complex (Figure 3). The first step is the separation of the solid phase from the liquid phase. A variety of solid–liquid separation technologies is available on the market. Screw press separators, decanter centrifuges and belt filter presses are most common for MOW digestate

processing (Raussen and Kern, 2016). Screw press separators are applied for digestate with high fiber content which is moved against a cylindrical sieve. The increasing diameter of the screw forces a pressure rise so that the liquid fraction is drained. The moisture content of the solid residue is reduced to 60% (Raussen and Kern, 2016). Decanter centrifuges and belt filter presses are used to treat digestates with a high moisture content (>90%). Through exploitation of centrifugal forces and utilization of flocculants, dewatering of solid remains is facilitated. In belt filter presses digestate is drained and process water is removed through pressing between filter belts. The solid digestate contains 25% to 40% of dry matter (Raussen and Kern, 2016). Screw press separators are popular due to low investment costs (Bauer et al., 2009) and low energy consumption (Fuchs and Drosg, 2013). However, sludge fractions, which are usually rich in phosphorus, cannot be separated from the liquid digestate by screw press separators. Consequently, Bauer et al. (2009) determined 69% of TN and 49% of P in the liquid fraction after separation in a screw press. Tambone et al. (2017) even found 87% of TKN and 71% of P_2O_5 in the liquid fraction after digestate separation. By using decanter centrifuges and belt filter presses a predominant share of phosphorus of up to 90% can be recovered in the solid residue (Møller et al., 2002). Depending on the fertilizing strategy of surrounding farms and soil requirements, the phosphorus distribution can be controlled by the separation technique applied (Al Seadi et al., 2013).

After separation, the solid phase can be either directly applied to agricultural land or further processed by drying or composting. MOW digestates are commonly composted after drainage, since the existing technologies and knowhow of aerobic waste treatment can be used for processing (Raussen and Kern, 2016). Furthermore, the quality requirements for MOW digestates are the same as for composts. Common composting technologies are windrow composting, rotting tunnels and line composting. To improve process performance and to accelerate substrate drying, compost material is aerated and turned over regularly. As solid digestate has a greater emission potential than fresh MOW especially with regard

to NH_3, roofing and air purification during composting are recommended (Raussen and Kern, 2016). Mixing the digestate with bulking agent is recommended (Bustamante et al., 2013), as it increases oxygen supply and self-heating potential and may also decrease N-emissions (Zeng et al., 2016). Finally, composted digestate is sieved to remove bulk material and impurities. For the agricultural utilization of composts, mesh sizes of 20 mm are applied (Raussen and Kern, 2016). To improve compost quality, wind sifter can be used. Moisture content of compost shall be 40% to 50% to ensure efficient separation and reduce sieve overflow (Raussen and Kern, 2016).

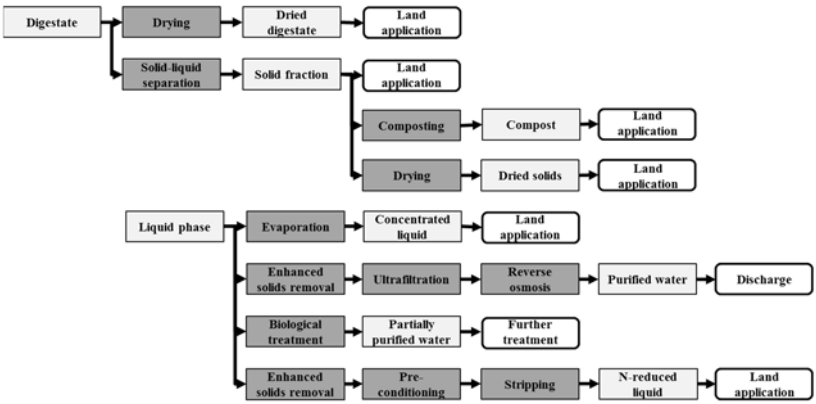

Figure 3: Overview of processes involved in treatment of solid and liquid digestates (Al Seadi et al., 2013)

Drying of solid digestates requires the supply of heat energy, which accounts for up to 1.6 kWh_{th} per liter H_2O (Raussen and Kern, 2016). Commonly, to keep energy costs low, waste heat from the digestion process or from the CHP unit shall be utilized (Drosg et al., 2015; Rehl and Müller, 2011). There are different drying technologies. Belt dryers, drum dryers and solar dryers are most relevant. In belt dryers, solid digestate is moved and aerated on perforated conveyor belts at a temperature of 80 °C to 120 °C. Drum dryers consist of a rotating tube, where the solid residue is turned at temperatures over 200 °C. Solar drying is carried

out in greenhouse-like halls with solar panels where the solid digestate is spread on the ground and treated by floor heating. In all drying procedures, exhaust air and condensates need to be captured and purified. Especially during the first days of drying high emissions need to be expected (Maurer and Müller, 2012). Furthermore, drying causes a significant loss of up to 80% of NH_4 in the digestate (Awiszus et al., 2018; Maurer and Müller, 2012). A comparison of drying opportunities for digestates revealed that belt dryers have the highest primary energy demand (Rehl and Müller, 2011).

Depending on the feedstock composition and the separation technology applied, the liquid fraction of digestates contains suspended solids and nutrients. It can be directly applied to soils as nitrogen-rich liquid fertilizer, partially reused as process liquid in the digestion process or be further conditioned. Processing mostly aims at nutrient recovery and water purification. There are different treatment technologies of which ammonia stripping, membrane filtration and evaporation are most relevant. Ammonia stripping (air stripping or vapor stripping) makes use of the volatility of NH_3, which is removed from the process liquid through a continuous gas flow. pH and temperature of digestate are increased to maximize recovery rates. pH is elevated by degassing of CO_2 or by the addition of alkali. NH_3 is transferred from the liquid digestate to the stripping gas stream and subsequently recovered by a sulphuric acid scrubber where ammonium sulphate is formed. During vapour stripping, ammonia is directly condensed to produce ammonia water. The advantage of ammonia stripping is that a nitrogen fertilizer product is obtained, which can be applied according to common fertilizer standards (Fuchs and Drosg, 2013). Membrane filtration is a separation process where liquid digestate passes membranes of different pore sizes. Pores retain particles and a purified permeate is produced. Depending on the pore size, membrane processes can be categorized in microfiltration (particles > 0.1 µm), ultrafiltration (colloids > 0.01 µm), nanofiltration and reverse osmosis (ions < 0.01µm, e.g. NH_4^+). There are two types of membranes. Porous membranes retain particles by size-exclusion. Solution-diffusion

membranes (e.g. ceramic membranes) absorb substances separated by differences in their diffusion velocity. Efficient solids removal is crucial for membrane purification processes to prevent membrane fouling. During evaporation, liquid digestate is heated above evaporation temperature (90 °C) in a heat exchanger and then circulated in a low-pressure evaporation vessel. Acidification of digestate reduces volatilization of NH_3 and ensures that nitrogen remains in the concentrate during processing. Condensate can be recycled in the biogas plant, further purified or discharged. The comparison of treatment options for liquid digestates shows that ammonia stripping is advantageous, as it does not require chemicals and high thermal energy expenditure and provides a marketable N-fertilizer. Membrane purification is the most expensive technology (Drosg et al., 2015). Moreover, it results in a significant amount of byproducts (e.g. retentate) from the process, which need to be recycled or discharged. Evaporation can be an interesting option if excess heat is available.

To sum up, it can be said that there exists a variety of treatment options for digestates. However, the market value of products is limited (Fuchs and Drosg, 2013) and advanced digestate processing requires high energy inputs and the deployment of chemical reagents. The quality of the digestates and local, site specific conditions have a strong influence on treatment costs (Delzeit and Kellner, 2013; Drosg et al., 2015). The implementation of treatment fails when processing costs exceed benefits from material and nutrient recovery. Furthermore, not all treatment technologies have already reached market maturity (Fuchs and Drosg, 2013). Solid-liquid separation and subsequent composting and purification of the solid phase are common treatment measures for MOW digestates. Thermal treatment is rarely applied (Möller and Müller, 2012). The processing of liquid digestates is still in the development phase and only a few specialized facilities exist in practice (Bauermeister, 2015; Fraunhofer-IGB, 2016). Still, in most cases the direct application of solid digestates is most efficient with regard to economic feasibility (Drosg et al., 2015; Fuchs and Drosg, 2013). However, in regions where the agricultural areas for digestate spreading

are scarce, processing of digestates increases the profitability of biogas production (Delzeit and Kellner, 2013). Currently, opportunities for digestate marketing are largely unexploited (Dahlin et al., 2015) and strategies to reach customers (farmers, horticulturists and private customers as well as fertilizer manufacturers) need to be established. Besides profitability, the quality of final fertilizer and amendment products is a crucial criterion for its credibility. Upgraded digestate products offer an increased marketability (Dahlin et al., 2015; Fuchs and Drosg, 2013). Stricter fertilization regulations and nutrient scarcity will force an increase of nutrient recovery measures in the future.

3 Scope of the thesis

3.1 The VeNGA Project

The practical work this thesis is based upon was examined during the research project Investigations on the production of an organic fertilizer using solid residues from anaerobic digestion of organic waste and its effect on plant growth and soil development (VENGA - Grundlagenuntersuchungen zur Verwertung und Nährstoffnutzung sowie zur boden- und pflanzenbezogenen Wirkung von Gärrückständen aus der Abfallvergärung, FKZ: 03EK3527A). This project wass conducted by the co-work of three partners: the Institute of Agricultural and Urban Ecological Projects Berlin (Institut für Agrar- und Stadtökologische Projekte, IASP), the company Grossmann Ingenieur Consult GmbH Dresden (GICON) and the Brandenburg University of Technology Cottbus-Senftenberg (Brandenburgische Technische Universität Cottbus-Senftenberg, BTU). It was carried out from July 2013 to December 2017. The German Ministry of Education and Research (Bundesministerium für Bildung und Forschung, BMBF) funded it. The main objectives of the project were to investigate properties of digestates from anaerobic treatment of municipal organic waste (MOW), to explore treatment measures and to evaluate the effects of digestate-based amendment products on plant and soil development. The overall goal of research was to provide marketable, high-quality amendment products that can be recycled onto agricultural land.

Within the project, anaerobic treatment of MOW was carried out in the two-stage digestion process of the company GICON, who has been a cooperation partner. The GICON process is the only industrial scale two-stage biogas process with discontinuous dry digestion of feedstocks. It was developed at BTU Cottbus and patented in 2006 (DE 10 2004 053 615 B3: Abbauverfahren von biogenem Material, GICON Verfahren). The biggest GICON biogas plant for the anaerobic treatment of MOW with a capacity of 30 000 tons year^{-1} was put into operation

in 2013 in Richmond, Canada. The GICON process is advantageous for MOW treatment for the following reasons:

- High impurity tolerance and subsequently low pretreatment effort (no impurity removal needed prior to digestion)
- Low wear susceptibility, no mixing of feedstocks
- Inoculation is realized by percolation (recycling of liquid digestate)
- High buffer capacity in the percolate prevents hyperacidity causing process inhibitions
- Milieu conditions within the digesters and the biogas production can be controlled by the management of percolate dosage
- High methane concentration in the biogas (> 70%)
- High dry matter content of digestates (20-30%), no solid-liquid separation needed
- No liquid digestates due to the recirculation of percolate

During the GICON anaerobic digestion procedure MOW is degraded by discontinuous dry fermentation with percolation (first stage) and subsequent treatment of process liquid in a fixed-bed digester for methanation (second stage). This separates acid fermentation and methanogenesis and enables the plant operator to optimize process conditions for microorganisms. Subsequently, pH and the hydraulic retention time of percolate differ in each stage. Therefore, the two-stage biogas plant may be less susceptible to process inhibition as the anaerobic digestion can be controlled with regard to the individual process performance of each stage. MOW is brought to the system in batch and remains in the box fermenters during treatment. The feedstock itself is not moved or mixed during the process. Solely, a sufficient substrate porosity is needed for percolate flow, which is ensured by coarse pre-shredding of MOW and by subsequent homogenization with organic bulk material. Percolate takes up dissolved compounds and is subsequently fed to the fixed-bed digester for methanation. Anaerobic digestion is run in the mesophilic temperature range. With the GICON process several box fermenters can be included and batches are

started at staggered times. Percolation in each box and feeding of the fixed-bed digester is separately controlled with regard to process monitoring. At the end of the digestion process digestate is drained and process liquid remains in the storage tanks of the biogas plant. Experiments regarding the effect of digestion on the properties of process residues have been done at laboratory and semi-industrial scale. A laboratory two-stage biogas plant was constructed at BTU. Industrial scale experiments were carried out by GICON in the company-owned technology center in Cottbus. A detailed description of process settings during the experiments of this dissertation is presented in the sections 4-6 (Materials & methods).

The investigated MOW feedstocks were provided by the company Becker Umweltdienste, which operates a composting plant in Burkersdorf/Frauenstein. MOW originated from separate collection (biowaste bins) in the vicinity of Freiberg close to Dresden, Germany. After collection, MOW was homogenized with a gripper, which also resulted in the ripping of waste bags. Subsequently, MOW was mixed with organic bulk material (mainly wood chips and branches, share of 10 to 15% of fresh matter). The final mixture was used in the laboratory biogas plant as well as in the GICON technology center.

After digestion, the post-treatment of process residues was investigated. At industrial scale, digestates were conditioned by composting. For this purpose, digestate was delivered to the composting plant in Burkersdorf, where it was treated in open heaps. In comparison to composting, digestate drying was investigated in the BTU laboratory. Furthermore, the efficiency of impurities removal by sieving, heavy metal distribution and the pelletisation of digestates was explored. Finally, digestate properties were characterized along the different steps of the processing chain in the BTU laboratory. The impact of digestate products on soil development and plant growth was investigated by pot experiments in the green house and during a three-year field trial. Results of amendment application are not subject of this thesis.

3.2 Sampling and data acquisition

A comprehensive overview of existing provisions for MOW sampling and analysis is presented in section 2.3 of this thesis. Samples of feedstocks, raw and conditioned digestates from the laboratory facilities, as well as from the semi-industrial scale experiments and from operating biogas plants were investigated by BTU. Amendment characteristics need to meet the requirements of the German Biowaste Ordinance (Bioabfallverordnung, BioAbfV). Consequently, criteria of BioAbfV were addressed during sampling, sample preparation and analysis.

Based on the results from the method review, a sampling and analysis strategy for relevant substrates was developed. Investigated batches were clearly heterogenic with particle sizes up to 120 mm and a volume of up to 30 m^3. All substrates were prepared and stored at the compost facility heaped up in piles (digestates from the laboratory biogas plant were sampled at BTU). Altogether all substrates were subject to following sampling measures:

- Sampling was examined at the composting facility according to instructions of LAGA PN98 (Länderarbeitsgemeinschaft Abfall/ Federal Working Group on Waste).
- Eight randomly distributed withdrawals per substrate pile were examined to receive a composite sample.
- The composite sample and BTU digestate was homogenized and reduced by quartering.
- Due to restricted laboratory capacities, two final laboratory samples of 5 liters were combined to one sample. Sample size of the laboratory sample after subsampling was 10 liters (5-8 kg).
- One laboratory sample was taken for each batch.
- One third of the laboratory sample was frozen.
- Two thirds (approx. 5 kg) of the laboratory sample were dried at 105 °C. Sample preparation was examined according to DIN 19747 and DIN EN 13567 (both LAGA recommendation).

- After impurity analysis (including sieving at 2 mm & 10 mm) and the removal of stones and impurities > 2mm, the complete dry laboratory sample (1-2 kg) was homogenized by shredding in a rotary cutting mill (grain size < 4 mm). This should ensure a representative result with regard to substrate heterogeneity of investigated samples.
- A subsample of 200 ml of the shredded sample was treated in a mortar grinder to receive an analysis sample with a grain size of < 250 µm.

Analysis of substrate parameters followed provisions of BioAbfV, LAGA method collection 3.0 (2016), the methods book (2014) of the German Federal Compost Association (Bundesgütegemeinschaft Kompost e.V., BGK) and the guideline VDI 4630 by the Association of German Engineers (Verein Deutscher Ingenieure, VDI). Details on analysis procedures are provided in sections 4-6.

3.3 Purpose and objectives of the thesis

Within the context of the research project VeNGA this thesis focuses on the influence of the anaerobic digestion and subsequent post-treatment on the properties of digestates from MOW treatment in the two-stage biogas plant. The main objectives are to understand how element contents of MOW change during treatment and how substance flows develop during processing. The knowledge gained shall be used to make clear what elements can be provided to soil by MOW-based amendments and what are potentials to improve recovery rates.

So far, research has mainly focused on improving the anaerobic treatment process with regard to biogas yields with minor interest in the digestate's quality. However today, due to legal restrictions for digestate spreading on agricultural land, digestate processing is becoming an essential part for successful plant operation and digestate properties gain importance with regard to marketing. To manage final amendment characteristics, it first needs to be clear how the biogas process affects digestate properties. A few studies investigate characteristics and fertilizing effects of digestates. However, most of them focus on untreated

digestates from single-stage wet fermentation of energy crops and manure. Little information is available about characteristics and effects of digestates from anaerobic treatment of MOW. No study is known, which investigates digestate development and the fate of nutrients and heavy metals in a two-stage biogas plant. Additionally, amendment properties of one digestate have not been related to different treatment procedures yet.

This thesis aims at closing the knowledge gaps on digestate properties as well as on mass flows and nutrient recovery potentials during MOW treatment in a two-stage biogas plant with subsequent post-treatment of digestion residues. Based on the literature review in section 2, following hypotheses shall be proven:

- Anaerobic digestion of MOW in the two-stage biogas plant significantly increases element concentration in the solid substrate. Phosphorus can mainly be recovered in the solid digestate.
- The accumulation of elements during anaerobic treatment is related to the retention time and degradation rate of MOW.
- Post-treatment of MOW digestates affects potential fertilizing performance of amendment products, in particular nutrient, heavy metal and carbon availability.
- A share of nutrients and heavy metals contained in the feedstock is lost during complete MOW treatment due to mineralization, deposition and volatilization of elements and material separation.

3.4 Organization of the thesis

This thesis presents the results of a cumulative doctorate. Section 2 gives a comprehensive review on the current state of research on properties and collection of MOW as well as on anaerobic treatment of MOW and possibilities for digestate conditioning.

Section 4 to 6 are organized as self-contained papers that were published in 2017 and 2018 in peer-reviewed scientific journals. These journals are:

- Bioresource Technology (section 4 and 6)
- Waste Management (section 5)

Each article is composed of a separate abstract, an introduction, a materials and methods section followed by the presentation and discussion of results. Section 7 presents a synthesis and conclusions based on all results obtained and will also reflect on the hypotheses given in section 3.3.

4 Nutrient and heavy metal accumulation in municipal organic waste from separate collection during anaerobic digestion in a two-stage laboratory biogas plant

This chapter was published as: Knoop, C., Dornack, C., Raab, T., 2017. Nutrient and heavy metal accumulation in municipal organic waste from separate collection during anaerobic digestion in a two-stage laboratory biogas plant. Bioresource Technology 239, 437–446. doi: 10.1016/j.biortech.2017.05.026

4.1 Abstract

Municipal organic waste (MOW) is a promising feedstock for biogas plants and separate collection will increase available quantities. To close nutrient circles digestates shall be redistributed to arable land. However, less is known about digestate properties and how they are influenced during digestion. Therefore, changes in nutrient and heavy metal concentration in the solid digestate were investigated during anaerobic treatment of MOW in a two-stage laboratory biogas plant. Results show that the solid digestate is exposed to element accumulation, except for N, P and Mg. The loss of initial N, P and Mg load accounts up to 45%, which must be redistributed elsewhere in the digester system. K load of feedstock was completely rediscovered in the solid digestate.

Heavy metal concentration in the digestate increases by factor 1.6 at average. The results emphasize that element retention in the digester system has a decisive impact on nutrient content of digestates.

4.2 Introduction

In the last decade, biogas has become an important energy provider. In 2016, 17% of electricity generation from renewable energies was delivered by the biogas sector in Germany (AGEE-Stat, 2016). Until today, more than 8000 biogas plants have been constructed in Germany (FNR, 2017) promoted by the refunding policy of the Renewable Energies Law (Erneuerbare-Energien-Gesetz, EEG). With the EEG amendments from 2012 to 2016 the German government clearly focussed on organic waste recovery. Because of this new subsidize policy, refunds for biogas from organic waste are higher than for biogas from energy crops. Another motivation for waste recovery is the introduction of a nationwide separate collection of municipal organic waste (MOW) in Germany in 2015 under the Closed Substance Cycle and Waste Management Act (Kreislaufwirtschaftsgesetz, KrWG). Different studies show that about 9 million tons of MOW, which can also be referred to as biowaste, could be provided by separate collection every year (Kern et al., 2012; Schüch et al., 2016). More than 100 biogas plants in Germany have specialized on the treatment of MOW (Kern et al., 2012). An increase of MOW utilization as feedstock is expected (Schüch et al., 2016). The exploitation of the energetic potential of MOW through anaerobic digestion will result in a certain amount of digestion residues that are available for further usage. The application of digestates as soil amendment can be an interesting alternative to traditional fertilizers as they are suitable to replace nutrients and organic matter (Insam et al., 2015; Nkoa, 2014; Odlare et al., 2015; Odlare et al., 2011). The quality of digestates is mainly influenced by the characteristics of feedstock (Al Seadi et al., 2013; Alburquerque et al., 2012b; Zirkler et al., 2014). Following, the element composition of the ingestate can be an indicator for the potential nutrient recovery (Campuzano and González-

Martínez, 2016). Residues from organic waste digestion are known to contain more micronutrients than residues from energy crops digestion (Schattauer et al., 2011). However, Teglia et al. (2011b) do not recommend direct use of digestates and application on land as soil amendment due to impurity contents. To obtain a high-quality product post-treatment of digestates is necessary (Al Seadi et al., 2013; Drosg et al., 2015). In Germany, final product requirements are determined by the German Biowaste Ordinance (Bioabfallverordnung, BioAbfV). The anaerobic digestion of organic waste can be realized by various technologies. Today, a strong preference of dry fermentation systems can be observed for biowaste in Germany because of technological improvements achieved during the last years of biogas boom and a high impurity tolerance. Therefore, a two-stage laboratory biogas plant with dry fermentation of feedstocks is investigated in this study. After digestion, residues are commonly separated into a liquid and a solid fraction (Fuchs and Drosg, 2013). Investigations on energy crops digestates show that the liquid fraction is rich in plant-available nitrogen and potassium (Drosg et al., 2015). It can be considered as a liquid fertilizer and be either spread directly or be further conditioned by e.g. ultra-filtration and reverse osmosis to receive higher nutrient concentrations (Fuchs and Drosg, 2013). The solid fraction is carbon-rich and contains phosphorus and other micro nutrients (Drosg et al., 2015; Insam et al., 2015). A few publications have dealt with digestate characterisation (Al Seadi et al., 2013; Teglia et al., 2011b; Zirkler et al., 2014). Others have studied the fate of nutrients during anaerobic digestion (Massé et al., 2007; Möller et al., 2010; Möller and Müller, 2012; Schattauer et al., 2011). However, little information is available about solid digestate characteristics from anaerobic treatment of MOW as these residues are usually composted and further processed before application to land. Insam et al. (2015) suggest that instead of only generating biogas more emphasis shall be put on operating biogas processes with the objective of producing a highly functional soil amendment. To manage final amendment characteristics, it first needs to be clear how the biogas process affects digestate properties. With this study, knowledge on the fate of nutrients and heavy metals in the solid

digestate during anaerobic treatment of MOW shall be improved. This is realized by continuous sampling of substrate during the digestion process and following chemical analysis of digestates. Knowledge gained shall be used to consider post-treatment of digestate with regard to its usage as organic soil amendment. This article therefore aims at showing properties of feedstocks and digestates from a two-stage laboratory scale biogas plant with dry fermentation of MOW, determining the development of nutrient and heavy metal content in the feedstock during the anaerobic digestion process and evaluating the impact of retention time and degradation rate on the digestate quality.

4.3 Materials and methods

4.3.1 Feedstock

Three different feedstocks of source-separated municipal organic waste (MOW 1–3) have been treated by anaerobic digestion in the laboratory two-stage biogas plant under strict process monitoring and regular digestate sampling. Feedstocks were obtained from a local composting plant near Dresden (Germany). Test series took place in February 2015 (MOW 1), October 2015 (MOW 2) and April 2016 (MOW 3). Prior to digestion, feedstock was mixed with organic bulk material. Large plastic bags and impurities were removed to avoid process disturbances. 52 kg, 47 kg and 52 kg (MOW 1–3) of prepared feedstock were digested during the test series. Feedstock characteristics are described in Section 4.4.1.

4.3.2 Digestion process

Investigations on feedstock development during anaerobic digestion were examined in a laboratory scale two-stage dry-wet biogas plant (Figure 4). With this plant design, hydrolysis and acidogenesis of feedstock is spatially separated from acetogenesis and methanogenesis of organic acids contained in the process liquid. MOW is given into a 100 l hydrolysis fermenter in batch and gradually rinsed by process liquid. Percolate is circulated in the biogas system and thereby

takes up organic acids and other process intermediates. A 80 l fixed-bed fermenter is subsequently fed by acid-loaded process liquid. Organic load is removed in the fixed-bed during the following process steps of acetogenesis and methanogenesis and process liquid is recirculated onto the feedstock. Recirculation of process liquid was dependent on the organic loading rate (measured as chemical oxygen demand) and ranged from 10 l day^{-1} in the beginning of each experiment to 72 l day^{-1} at the end of each experiment. Additionally, internal circulation in the hydrolysis and fixed-bed digester was 70 l day^{-1}. Process temperature was 35–37 °C in the hydrolysis and 37–38 °C in the fixed-bed fermenter.

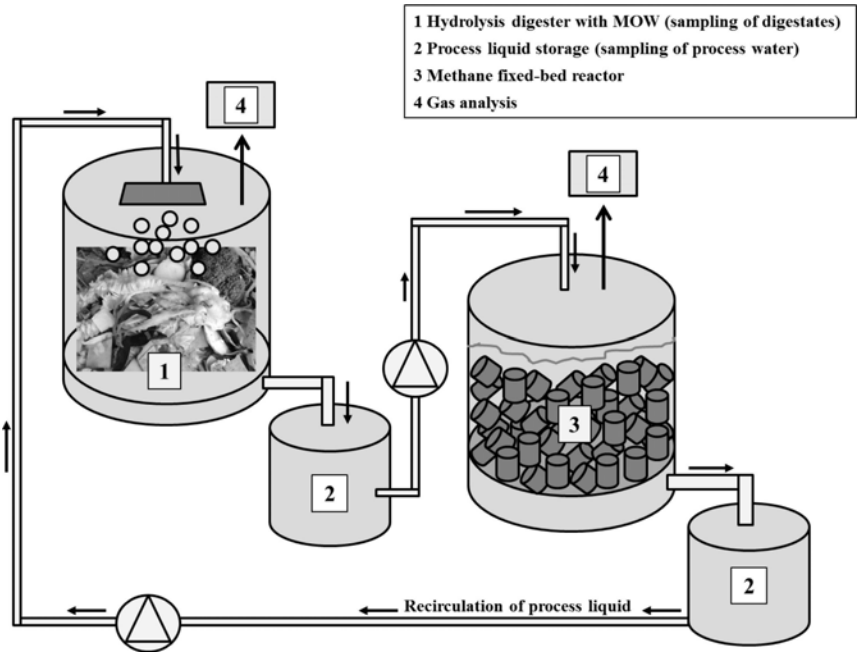

Figure 4: Setup of the two-stage laboratory biogas plant

To monitor the biogas process, samples of process liquid were taken every day during the first week of the experiment and every second day afterwards. The

amount and composition of biogas developed was measured daily (ANSYCO Biogas Analyser 5000). pH in the hydrolysis digester ranged from 5.8 to 7.8 and from 7.2 to 8.1 in the fixed-bed digester. Methane yield was 66%, 52% and 56% of methane potential (MP) (MOW 1–3). Retention time of feedstock was determined by the daily biogas generation. Abort criterion was reached when daily biogas production of the laboratory plant was below 3% of total biogas production during the batch experiment. Retention time of feedstock was 32, 27 and 28 days (MOW 1–3). An organic matter degradation rate of 60%, 56% and 62% (MOW 1–3) was reached during the experiments. After digestion, the hydrolysis fermenter was emptied and the leftover digestate was weighed. Process liquid remained in the storage tanks for following experiments.

4.3.3 Sampling of MOW and digestates

Feedstocks were sampled at the composting plant. To ensure representative sampling, up to 10 single samples of each batch were randomly taken and mixed to receive a representative composite sample, which was subsequently homogenized and reduced to a sample size of 3–5 kg. Fresh samples were subsequently prepared for lab analysis. Digestate sampling was done three times a week at the laboratory biogas plant. Therefore, the hydrolysis fermenter was opened manually and a fresh digestate sample of 1–2 kg was randomly taken. One third of the fresh sample was left untreated and stored in the freezer. The rest was dried at 105 °C, impurities >2 mm were removed and the leftover sample was shredded in a laboratory cutting mill and subsequently grounded in a mortar mill. The grounded sample was homogenized by sieving at 0.25 mm. Altogether during three examinations, each with the same experimental setup and three MOW feedstocks, 34 samples (= n) have been investigated.

4.3.4 Lab analysis of samples

The following parameters were determined in the fresh feedstock and digestate samples: pH after 1 hour extraction with $CaCl_2$, water content after 24 hours drying at 105 °C (DIN EN 13040) and methane potential (MP) according to

guideline 4630 of VDI (2006). Experimental setup of MP tests was done as described by Herrmann et al. (2011). Inoculum sludge was prepared as recommended by VDI (2006) and adapted to MOW feedstock during previous batch tests. Glass vessels were tempered at 37 °C in a heating oven. Tests were performed in duplicate. Gas composition (CH_4, CO_2, O_2) was measured with a gas meter (ANSYCO, Biogas 5000). Data evaluation and MP calculation was done according to VDI (2006).

The dry and grounded sample was used for the determination of volatile solids (VS) (DIN EN 13039) after 3 hours of ignition at 550 °C in a muffle furnace, organic carbon (C_{org}) as well as N and S after combustion in an automatic CNS-Analyser (Vario EL III). Nutrient content (P, K, Ca, Mg) and heavy metal content (Cd, Cr, Cu, Ni, Zn, Pb) was determined after pressure extraction in aqua regia (DIN EN 13650) using ICP-OES (Thermofisher Scientific, ICAP 6300 Duo, DIN EN ISO 17294-2). Analyses were carried out in duplicate. All values refer to the dry matter (DM).

4.3.5 Evaluation of results

Raw data was checked for normal distribution by Kolmogorov-Smirnov test and for outliers by Dixon's Q test (Ellison et al., 2009). Data was subsequently used to determine accumulation factors (E_{acc}) for each investigated element with following equation:

$$E_{acc} = \frac{c_{digx}}{c_{feed}}$$

Equation 1: Accumulation factors (E_{acc}); E = Element; c_{digx} = element concentration of digestate sample on day x; c_{feed} = element concentration of feedstock

A linear regression analysis has been conducted with E_{acc} of each element to evaluate nutrient and heavy metal development in the digestate during retention in the fermenter. Trendline equations were used to calculate mean E_{acc} in the digestate after 32, 27 and 28 days (MOW 1–3). Mean E_{acc} was compared to maximal possible accumulation (F_{100}). F_{100} is based on the DM degradation of feedstock. If mean $E_{acc} = F_{100}$, then we assume that all nutrients and heavy metals contained in the feedstock remain in the solid digestate. F_{100} for each batch was calculated as follows:

$$F_{100} = \frac{DM_{feed}}{DM_{dig}}$$

Equation 2: F_{100}; DM_{feed} = feedstock input in kg DM; DM_{dig} = digestate output in kg DM

A difference between E_{acc} and F_{100} indicates a loss of elements from the solid digestate during anaerobic treatment. It was determined using the following equation:

$$Loss\ [\%] = \frac{(E_{acc} - F_{100}) * 100}{F_{100}}$$

Equation 3: Element loss

It was not possible to weigh the solid digestate in the fermenter during treatment. Therefore, the digestate weight was calculated under two assumptions: organic dry matter is degraded by 30% after ten days of retention, which was found during investigations on MOW digestion in a two-stage semi scale biogas plant identical in construction (Pilot plant Cottbus, Germany), and the organic matter degradation is linear. With knowledge of the input weight, organic DM degradation after ten days and output weight as well as DM and VS content of digestate samples, the weight of digestate in the fermenter during treatment was determined.

To relate element accumulation (E_{acc}) to the MP of the remaining substrate in the digester (MP_{rem}) data obtained during MP test and sample analysis were used in following calculation:

$$MP_{rem}\ [Nl] = MP_{digx} * DM_{digx} * VS_{dig}$$

Equation 4: Methane potential of remaining substrate (MP_{rem}); MP_{dig} = Methane potential of digestate sample in Nl kg^{-1} VS; DM_{digx} = dry matter left in the digester on day x in kg, VS_{dig} = volatile solids content of digestate in % DM.

Subsequently, the calculated MP_{rem} was set into relation to initial MP of feedstock (MP_{feed}) to determine the MP_{rem} factor (F) using following equation:

$$MP_{rem\ F} = \frac{MP_{rem}}{MP_{feed}}$$

Equation 5: MP_{rem} factor

To evaluate dependency of $MP_{rem\ F}$ and E_{acc} a correlation analysis was examined.

4.4 Results and discussion

4.4.1 Characteristics of MOW feedstocks

Prior to the experiment initial characteristics of MOW from separate collection have been determined. Results are presented in Table 3. Characteristics differ between the three feedstocks. Total nitrogen (N) content ranges from 17 g kg^{-1} DM (MOW 1) to 21 g kg^{-1} DM (MOW 2). Phosphorus (P) content is highest in MOW 3 (3 g kg^{-1} DM). Potassium (K) concentration ranges from 9 g kg^{-1} DM to 12 g kg^{-1} DM in the feedstock samples. Calcium (Ca) content is highest for MOW 3 (21 g kg^{-1} DM) and lowest for MOW 2 (19 g kg^{-1} DM). Magnesium (Mg) concentration determined in the samples is 3 g kg^{-1} DM. Sulphur (S) content ranges from 2 g kg^{-1} DM (MOW 1) to 5 g kg^{-1} DM (MOW 3). Altogether, MOW 2 has the highest nutrient content. However, this is not the case regarding all single elements. The N and P content of MOW samples investigated is lower compared to the average findings of Campuzano and González-Martínez (2016) who reviewed the results of over 30 studies on MOW from all over the world. However, the summary of Campuzano and González-Martínez (2016) also shows a high variance in organic waste properties caused by regional peculiarities. Determined values are close to the findings of Hansen et al. (2007) who investigated 40 different source-separated organic waste samples from Danish cities. They determined an average N, P and K content of 2.5%, 0.4% and 0.9% of DM.

Heavy metal contents of feedstocks investigated also vary. Differences between the samples are bigger than for nutrient contents. Highest heavy metal concentrations in all samples can be found for zinc (Zn) and lead (Pb). This suits the findings of Smith (2009) who states the same for composts from municipal solid waste. Zn values determined range from 130 mg kg^{-1} DM (MOW 1) to 343 mg kg^{-1} DM (MOW 3). Pb content is highest in MOW 3 (189 mg kg^{-1} DM) and lowest in MOW 1 (32 mg kg^{-1} DM).

Table 3: Properties of MOW feedstocks (batches 1-3)

Parameter	Unit	MOW 1	MOW 2	MOW 3	Mean
N	g kg^{-1} DM	16.6	20.9	17.7	18.4 +/- 2.2
P		1.8	3.0	3.1	2.7 +/- 0.7
K		12.3	12.2	11.1	11.9 +/- 0.6
Ca		19.8	18.7	20.9	19.8 +/- 1.1
Mg		2.5	2.8	3.1	2.8 +/- 0.3
S		2.0	3.9	4.8	3.6 +/- 1.4
Sum of nutrients		55.0	61.5	60.8	59.1 +/- 3.6
Cd	mg kg^{-1} DM	0.8	0.7	1.8	1.1 +/- 0.6
Cr		13.2	12.2	18.9	14.7 +/- 3.6
Cu		20.0	19.5	46.6	28.7 +/- 15.5
Ni		6.5	7.1	9.9	7.8 +/- 1.8
Pb		32.4	49.2	188.8	90.1 +/- 85.9
Zn		129.7	206.8	343.4	226.6 +/- 108.2
Sum of heavy metals		202.5	295.4	609.4	369.1 +/- 213.2
pH		5.4	5.2	4.9	5.2 +/- 0.2
DM	% FM	33.4	26.8	31.6	30.6 +/- 3.4
VS	% DM	77.4	81.6	72.4	77.1 +/- 4.6
C_{org}	% DM	38.1	42.1	36.0	38.7 +/- 31.2
Impurity content	% DM	5.4	5.5	9.1	6.7 +/- 2.1
MP	Nl kg^{-1} VS	410	410	316	386 +/- 49

No big difference can be found for nickel (Ni) contents of feedstocks (7 mg kg^{-1} DM in MOW 1 and 2, 10 mg kg^{-1} DM in MOW 3). Copper (Cu) content of feedstocks ranges from 20 mg kg^{-1} DM (MOW 1 and 2) to 47 mg kg^{-1} DM (MOW 3). Chromium (Cr) concentration ranges from 12 mg kg^{-1} DM (MOW 2) to 19 mg kg^{-1} DM (MOW 3). The determination of cadmium (Cd) in the feedstocks

resulted in highest concentrations found for MOW 3 (1.8 mg kg^{-1} DM) and lowest concentrations found for MOW 2 (0.7 mg kg^{-1} DM). The thresholds set by the German BioAbfV are exceeded by the samples of MOW 3. The sum of heavy metals of MOW 3 is more than twice the sum of heavy metals of MOW 1 and 2. Additionally, the impurity content of MOW 3 (9.1%) is higher than in the other feedstocks.

Different authors (Amlinger et al., 2004; Kupper et al., 2014; Smith, 2009) emphasize that impurities highly contribute to heavy metal contamination. Especially batteries, metals and electronic scrap contain a broad range of heavy metals. Heavy metals can also be present in plastic bags (Huerta-Pujol et al., 2010), ink and paint (Smith, 2009). On-site miss-sorting is the main reason for impurity contamination of MOW. The maximum impurity content of organic amendments required by BioAbfV is 0.5% of DM. Results determined for MOW samples are all above this threshold. The high impurity content of MOW 3 may be the cause for its high heavy metal contamination. Furthermore, MOW 3 has the highest ash content, which indicates a higher share in minerals that may contain heavy metals. An important source for heavy metals are fine particles such as soil and dust contained in hoover bags, road sweepings and gardening waste (Smith, 2009; Veeken and Hamelers, 2002). The reduction of heavy metal content in MOW can be achieved by impurity removal during pretreatment. This is commonly done by sieving and metal separation. However, finely divided components are difficult to remove as they pass sieves and can be embedded in the organic matter (Smith, 2009). Investigations of Kupper et al. (2014) show that heavy metal contamination of feedstocks seem to occur at random. However, these contamination hot spots decrease overall MOW quality. As removal possibilities are limited, the impurity content of MOW feedstocks shall be low to ensure the production of a high-quality amendment during treatment (Kern et al., 2012).

pH of feedstocks is slightly acidic (from 4.9 for MOW 3 to 5.4 for MOW 1) which resembles the findings of Campuzano and González-Martínez (2016) and is also

typical for ensilaged energy crops (Herrmann et al., 2011). It shows that degradation processes already started during feedstock storage. Acidic conditions in the feedstock favour heavy metal availability and following redistribution (Smith, 2009). Dry matter (DM) content of MOW samples ranges from 27% (MOW 2) to 33% FM (MOW 1). The share of DM in the feedstock depends on the waste composition, which is mainly influenced by collection system and season (Hansen et al., 2007; Kern et al., 2012). Feedstocks with DM contents above 20% are suitable for dry fermentation, which is the preferred technique for anaerobic treatment of MOW today (Kern et al., 2012). The content of volatile solids (VS) in the feedstock samples ranges from 72% of DM (MOW 3) to 82% of DM (MOW 2) indicating a high share of digestible fractions. However, results of this study are below findings of Campuzano and González-Martínez (2016) who summarized an average VS content of 84% for MOW. In comparison, energy crops used as biogas feedstock have a higher VS (>90% DM) than MOW (Herrmann et al., 2011). Organic carbon (C_{org}) is highest in MOW 2 (42% DM) and lowest in MOW 3 (36% DM).

4.4.2 Development of methane potential of solid digestates during the experiment

Methane potential (MP) of MOW feedstocks investigated ranges from 316 Nl kg^{-1} VS (MOW 3) to 410 Nl kg^{-1} VS (MOW 1 and 2). This is in line with results of Davidsson et al. (2007) who determined a MP of 17 different MOW in batch tests operated at 55 °C of 300–570 Nl kg^{-1} VS. However, these results also show a great variability of MP, which is dependent on composition and degradability of organic waste (Davidsson et al., 2007). MP of MOW samples is higher than MP of ensilaged energy crop feedstock as determined by Herrmann et al. (2011).

The development of the MP of digestate samples is presented in Figure 5. The MP of the remaining substrate (expressed as ratio of MP of digestate and MP of feedstock = $MP_{rem\ F}$) in the hydrolysis digester is decreasing with increasing retention time and degradation of feedstocks ($R^2 = 0.85$, $p > 0.05$).

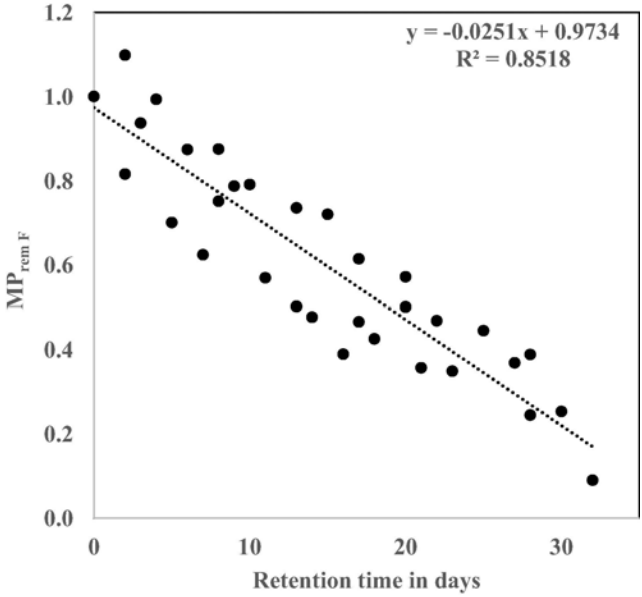

Figure 5: Residual methane potential ($MP_{rem\ F}$) of substrate sampled during digestion in the laboratory biogas plant

4.4.3 Changes of nutrient content in the digestate during anaerobic digestion in the two-stage laboratory fermenter

The nutrient content in the solid digestate during anaerobic treatment in the two-stage laboratory biogas plant is evaluated in this section. In general, it can be expected that nutrients are mineralized and solubilized during anaerobic degradation of organic compounds (Möller and Müller, 2012) is mainly contained in proteins and is mineralized to NH_4^+ during amino acid degradation. Furthermore, elemental S is reduced to HS^-, S^{2-} and H_2S (Chen et al., 2008). P, Mg, Ca and K contained in the feedstock are mineralized to PO_4^{3-}, Mg^{2+}, Ca^{2+} and K^+ (Möller and Müller, 2012). The high binding affinity of free cations and anions leads to the formation of new, stable compounds, which precipitate as sulfides, phosphates or carbonates (Möller and Müller, 2012). Main salts developing during anaerobic digestion are: struvite ($(NH_4)Mg[PO_4]$) and other phosphates, such as Ca-phosphate ($Ca_3(PO_4)_2$) or Fe-phosphate ($FePO_4$),

ammonium carbonate ($(NH_4)_2CO_3$), calcite ($CaCO_3$) and metal sulfide (Banks et al., 2011; Chen et al., 2008; Möller and Müller, 2012). Further possibilities for the retention of dissolved nutrients are the sorption to organic or inert solid particles in the digestate or in the process liquid (Möller and Müller, 2012). Microorganisms can also take up dissolved nutrient ions. Especially phosphate is essential for the building of cell substances (ATP, ADP). A share of N and S is volatilized to NH_3, NO_x and H_2S.

Figure 6 presents accumulation factors (E_{acc}) obtained from nutrient analysis of digestate samples. The highest nutrient contents were quantified for N, K and Ca. Lowest values were determined during analysis of P, Mg and S. The concentration of N, P and Mg in the solid digestate remains relatively constant during digestion. The gradient of the trendline does not significantly differ from 0. This implies that dissolved N, P and Mg ions from the feedstock are retained elsewhere in the fermenter system. It is known that if N, P and Mg ions are available in a solution in equal molar concentration struvite is formed (Le Corre et al., 2009). At the end of the experiment salt crystals were found on the floor of percolate storage tanks and in pipes. It is therefore assumed that dissolved P, N and Mg ions precipitated as struvite outside the hydrolysis digester. Struvite formation starts at pH of 5.5 and its solubility decreases with increasing pH (Le Corre et al., 2009). Booker et al. (2010) found that the highest amount of moles removed from wastewater was at pH 8.8–9.4. Furthermore, struvite formation has preferentially been observed in areas of high turbulence (Le Corre et al., 2009). Summarizing, the availability and bonding of nutrients is highly dependent on the pH (Möller and Müller, 2012). It can be expected that the acidic pH in the feedstock during storage and the first days of digestion leads to a release of ions. With increasing pH, the formation and precipitation of salt crystals is favored. pH change in the two-stage system happens when acidic process liquid is dosed to the methane digester and during recirculation of pH-neutral process liquid into the hydrolysis digester.

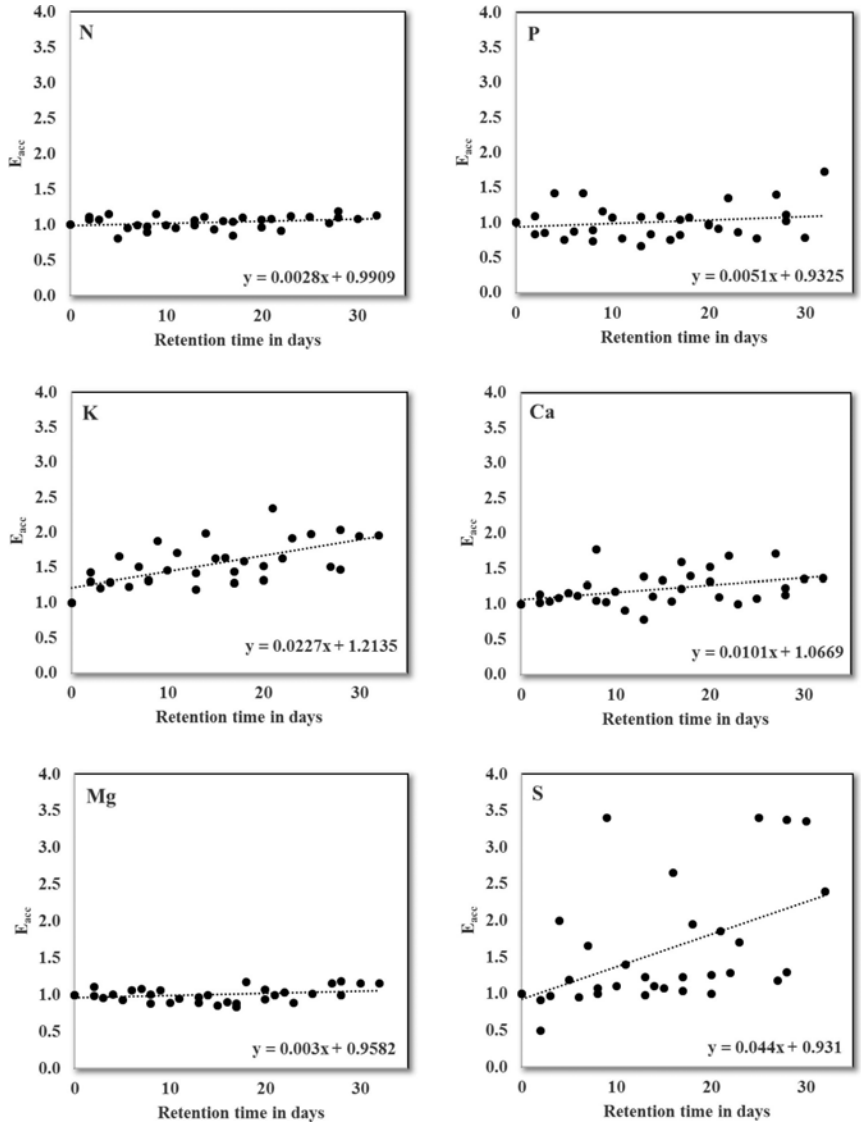

Figure 6: Development of nutrient content in the digestate (E_{acc}) during retention in the laboratory biogas plant

K, Ca and S accumulate in the remaining digestate during the experiment ($p < 0.05$). Highest gradient of trendline is found for S_{acc} and K_{acc} (Table 4). However, conclusions regarding the development of S in the digestate shall be made carefully as variance of S_{acc} is highest (SD of residuals = 0.71). Strongest positive correlation between retention time and nutrient accumulation was found for K_{acc} (R = 0.66).

Table 4: Results of regression analysis for nutrient accumulation (E_{acc}) and retention time as well as MP of remaining solid digestate (MP_{rem})

	N_{acc}	P_{acc}	K_{acc}	Ca_{acc}	Mg_{acc}	S_{acc}
R (Retention time)	0.30	0.20	0.66	0.40	0.29	0.52
R^2	0.09	0.04	0.44	0.16	0.09	0.27
Residual SD	0.09	0.24	0.25	0.24	0.25	0.71
Gradient of trendline	0.003	0.005	0.023	0.010	0.003	0.044
p-value	0.08	0.25	0.00	0.02	0.09	0.00
R (MP_{rem})	-0.24	-0.13	-0.70	-0.23	-0.31	-0.50

This indicates that K concentration significantly increases in the digestate during the experiments. From other investigations on digestates it is known that the liquid phase of digestates is rich in K (Drosg et al., 2015) leading to the conclusion that the release of K^+ during anaerobic digestion is high. During investigations on nutrient concentrations in a single-stage full scale biogas plant, Zirkler et al. (2014) also found that K concentrations in the fully-mixed digestate remain constant over time indicating that there is no deposition of K in the biogas plant. Furthermore, the assessment of K dynamics in soil shows that K^+ originating from the decomposition of organic matter replace other cationic species (Mengel, 2007). This is caused by the lower hydration energy of K^+, making the bonding with water less strong than for other hydrated cations (Mengel, 2007). By regular percolation during digestion K^+ may be stripped of its hydration water and thereby enrich in the solid digestate over time. This is also underlined by

Chen et al. (2008), who state that K serves as an important extractant for cations bound to exchangeable sites in sludge.

4.4.4 Changes of heavy metal content in the digestate during anaerobic digestion in the two-stage laboratory fermenter

Figure 7 presents the results obtained for the development of heavy metal concentrations in the solid digestate samples. Highest values were measured in the dry sample for Zn, Pb and Cu. Lowest values have been determined for Cr, Cd and Ni. The concentration of all heavy metals is increasing in the solid digestate during anaerobic treatment ($p < 0.05$) (Table 5).

Table 5: Results of regression analysis for heavy metal accumulation (E_{acc}) and retention time as well as MP of remaining solid digestate (MP_{rem})

	Cd_{acc}	Cr_{acc}	Cu_{acc}	Ni_{acc}	Pb_{acc}	Zn_{acc}
R (Retention time)	0.59	0.71	0.48	0.75	0.63	0.80
R^2	0.34	0.51	0.24	0.56	0.40	0.64
Residual SD	0.18	0.17	0.74	0.18	0.19	0.13
Gradient of trendline	0.014	0.019	0.044	0.022	0.016	0.019
p-value	0.00	0.00	0.00	0.00	0.00	0.00
R (MP_{rem})	-0.57	-0.62	-0.46	-0.63	-0.48	-0.79

The gradient of the trendline is highest for Cu_{acc} (0.04). However, standard deviation of residuals is also highest for Cu_{acc}, indicating a high variance of determined results. Strongest positive correlations between heavy metal accumulation and retention time can be found for Zn_{acc} (R = 0.80), Ni_{acc} (R = 0.75) and Cr_{acc} (R = 0.71). The correlation between heavy metal accumulation in the digestate and retention time is higher than between heavy metal accumulation and methane potential of remaining digestate ($MP_{rem\ F}$). It is also stronger than determined for nutrient development (Section 4.4.3). This

indicates that heavy metal accumulation in the solid digestate is more dependent on the retention time than on the rate of substrate degradation (as expressed by $MP_{rem\ F}$, Section 4.4.2).

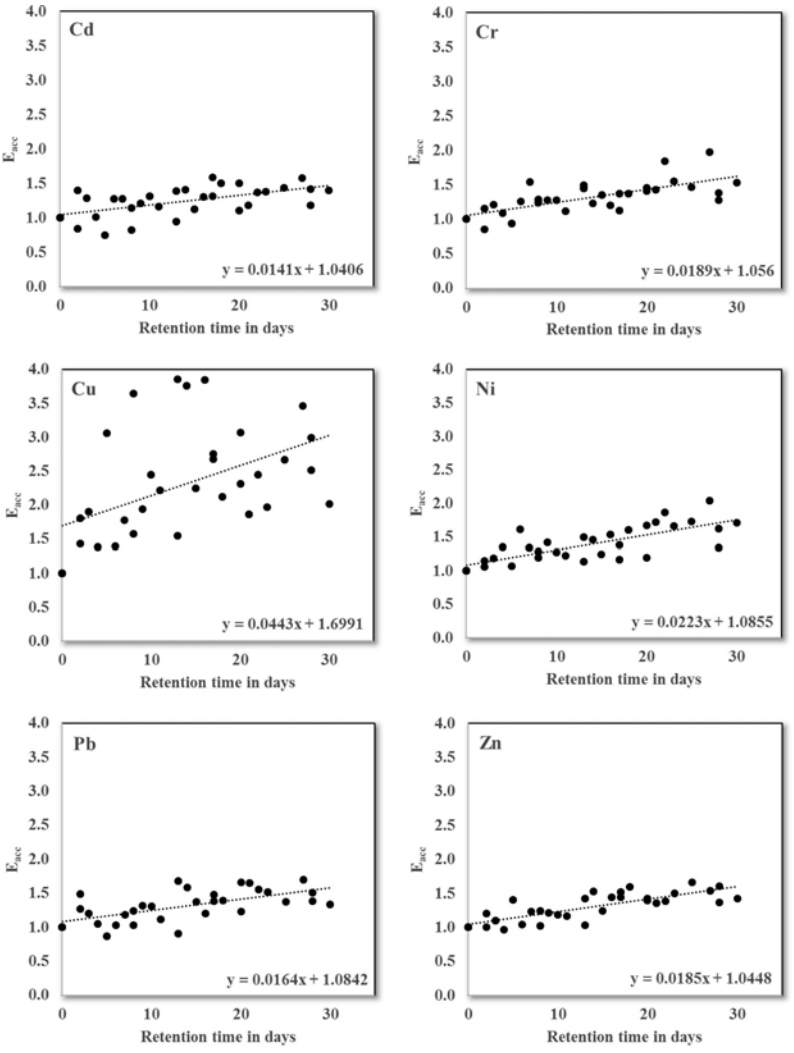

Figure 7: Development of heavy metal content in the digestate (E_{acc}) during retention in the laboratory biogas plant

The availability of heavy metals in organic waste, digestates and composts is highly dependent on pH, salt content, organic matter decomposition and total element concentration (Smith, 2009). As a low pH favours heavy metal availability, an increased mobility of heavy metals can be expected during storage and the first days of experiment due to acidification of feedstock. Process liquid analysis for Cu, Zn, Pb during the first experiment confirms this. Dissolved heavy metal cations (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Cr^{2+}, Pb^{3+}) are available for the formation of new bonds in the digester system. Principally, different possibilities for metal ion bonding during anaerobic treatment exist: metal precipitation (as sulfide, phosphate and carbonate) and sorption or complexation with organic and inorganic compounds (Callander and Barford, 1983; Möller and Müller, 2012). Precipitation of heavy metals depends on the availability of anions such as S^{2-}, CO_3^{2-}, PO_4^{3-}. Sulfide anions are important receptors for heavy metal cations causing metal sulfide precipitation (Lewis, 2010). Sulfur concentration in the feedstock is up to 5 g kg^{-1} DM. As sulfur concentration in the digestate rises over time, metal sulfide precipitation can be one explanation for heavy metal enrichment in the solid digestate.

Additionally, heavy metal increase in the digestate can be caused by complexation with residual organic compounds. Complexing agents contain functional groups that have an affinity for metal ions (Callander and Barford, 1983). They reduce free metal ions in the process liquid and can thereby even diminish precipitation (Möller and Müller, 2012). Complexation leads to the development of finely dispersed precipitates. It may be possible that by continuous percolation these precipitates settle in the solid digestate, which acts as a filter. As complexation plays an important role for the bioavailability of heavy metals (Möller and Müller, 2012), this may be another reason for heavy metal enrichment in the solid digestate. Finally, heavy metal accumulation is caused by the reduction of organic dry matter due to degradation. Little is known about the bioavailability of heavy metals in digestates. Knowledge on heavy metal availability and binding forms was mainly gained during investigations on composting as well as on aerobic and anaerobic treatment of sewage sludge

(Amlinger et al., 2004; Fuentes et al., 2006; Smith, 2009; Walter et al., 2006). Chemical extractability of heavy metals decreases with the duration of organic matter degradation (Smith, 2009). Although the concentration of heavy metals in the digestate rises, the leaching potential can be expected to be lowered during digestion due to increasing maturity of organic matter and the formation of stable metal complexes.

4.4.5 Evaluation of element accumulation in the digestate

Based on the determined trendlines for single elements development during digestion (Sections 4.4.3 and 4.4.4), mean nutrient and heavy metal accumulation of initial element concentration in the solid digestate can be calculated and evaluated. In Table 6 mean accumulation of investigated elements (E_{acc}) of MOW 1–3 is presented. These figures are compared to the highest possible accumulation during digestion (F_{100}) in which case 100% of nutrients and heavy metals contained in the feedstock would retain in the solid digestate. Differences between mean accumulation and mean F_{100} can be considered as lost from the solid digestate and as redistributed elsewhere in the digester system (either dissolved or deposited).

The highest element accumulation factors have been found for K (1.9), S (2.2), Cu (3.0) and Ni (1.7). Lowest factors have been determined for N (1.1), P (1.1) and Mg (1.1). Subtracting mean F_{100} from each element accumulation factor shows that loss of N, P and Mg from the solid digestate in the hydrolysis fermenter accounts for 43–45%. Accumulation of initial heavy metal concentration in the hydrolysis digester ranges from 1.5 (Cd) to 1.7 (Ni). However, comparison to F_{100} indicates that up to 24% (Cd) of the initial heavy metal load from the feedstock is lost from the solid digestate, indicating a redistribution of heavy metals in the digester system. Initial K load of feedstock can be fully rediscovered in the solid digestate as the K accumulation factor resembles F_{100}. Accumulation of S and Cu lies above F_{100}, which means that the final load of digestate is higher than the initial load of the feedstock.

Table 6: Mean nutrient and heavy metal accumulation in the digestate (initial element concentration = 1.00), Element loss in the solid digestate during anaerobic treatment (calculated as mean difference from F_{100})

Element accumulation by factor			Element loss [%]		
	Mean	**SD**		**Mean**	**SD**
N	**1.07**	0.01	N	**-43.8**	1.6
P	**1.08**	0.01	P	**-43.4**	1.5
K	**1.87**	0.06	K	**-1.9**	2.4
Ca	**1.36**	0.03	Ca	**-28.7**	1.7
Mg	**1.05**	0.01	Mg	**-45.2**	1.6
S	**2.21**	0.12	S	**15.6**	4.2
Cd	**1.45**	0.04	Cd	**-24.0**	1.8
Cr	**1.60**	0.05	Cr	**-15.9**	2.1
Cu	**2.98**	0.12	Cu	**56.4**	4.3
Ni	**1.73**	0.06	Ni	**-9.2**	2.3
Pb	**1.56**	0.04	Pb	**-18.3**	1.9
Zn	**1.58**	0.05	Zn	**-17.1**	2.0
F_{100}	**1.91**	0.06			

The S increase cannot be explained as there is no additional source of S in the digester system. As the variability of S_{acc} is high (SD of residuals = 0.7) this result may be caused by selective S distribution in the digestate resulting in samples with higher S contamination. Cu_{acc} also shows a higher variance. However, surplus may be caused by Cu leaching from the digester fittings and hose connections made of brass. Corrosion of brass was detected during the duration of the experiments.

As already investigated in Sections 4.4.3 and 4.4.4, dissolved nutrient and heavy metal ions can be assumed to form new compounds, to attach to organic matter or to be taken up by microorganisms. During this experiment, nutrient and heavy

metal redistribution during anaerobic digestion leads to a loss of initial element load (except for K, Cu and S) in the solid digestate. Similar results were found by Banks et al. (2011) during a study on the digestion of domestic food waste, where a loss of N and P (up to 70% of initial load) in the digestate due to precipitation was detected. Massé et al. (2007) also reported a loss of initial P, Ca, Cu, Zn and S fed to a PASBR for pig manure digestion. Zirkler et al. (2014) found that retention was highest for N and Mg, but also for P and Ca during co-digestion of food waste and pig slurry. Results of this and other studies emphasize that element retention in the digester system impacts on final digestate characteristics. However, the dimension of element retention varies and seems to be depending on element composition of feedstock and process conditions during digestion. Table 7 shows final digestate characteristics of MOW 1–3. MOW digestates from two-stage digestion contain an average nutrient content in the DM of 2.0% N, 0.4% P, 2.0% K, 2.8% Ca, 0.3% Mg and 0.5% S. Heavy metal load of MOW digestates of this study varies significantly. Overall, heavy metal contents determined for MOW digestates 2 and 3 are higher than in a study on MOW digestates by Govasmark et al. (2011). Cr and Ni contents of MOW digestates are similar to the findings of Govasmark et al. (2011). Apparently, higher contamination of MOW digestates with Zn, Pb and Cd is caused by high initial heavy metal content of feedstocks (see Table 3). Digestate of MOW 3 exceeds legal thresholds of BioAbfV for Cd, Cu, Pb and Zn. It would therefore not be suitable as soil amendment. This underlines the importance of feedstock quality. As the degradation of the organic fraction during waste treatment leads to further accumulation of heavy metals, a low contamination of feedstocks is desirable. The pH of solid digestates is slightly alkaline (Mean = 7.6) which indicates an improved biological stability. DM content of solid digestate after drainage of process liquid is 28% at average. For post-treatment of solid digestates a low water content is favourable as dewatering is highly energy consuming and costly. VS (Mean = 60% of DM) and C_{org} (Mean = 33% of DM) of MOW digestates have been significantly reduced during anaerobic treatment.

Table 7: Characteristics of solid MOW digestate (batch 1-3)

Parameter	Unit	MOW 1	MOW 2	MOW 3	Mean
N	g kg^{-1} DM	18.8	21.3	19.4	19.8 +/- 1.3
P		3.1	4.3	3.5	3.6 +/- 0.6
K		23.9	18.3	16.4	19.5 +/- 3.9
Ca		27.0	32.1	23.5	27.5 +/- 4.3
Mg		2.9	3.2	3.1	3.1 +/- 0.2
S		4.8	4.6	6.2	5.2 +/- 0.9
Sum of nutrients		80.5	83.8	72.1	78.8 +/- 6.0
Cd	mg kg^{-1} DM	1.1	1.1	2.1	1.4 +/- 0.6
Cr		20.2	24.1	24.2	22.8 +/- 2.3
Cu		40.4	67.4	117.0	74.9 +/- 38.9
Ni		11.0	14.5	13.3	12.9 +/- 1.8
Pb		43.1	83.3	262.0	129.5 +/- 116.5
Zn		185.0	318.9	470.3	324.7 +/- 142.8
Sum of heavy metals		300.7	509.3	888.9	566.3 +/- 298.2
pH		8.1	7.3	7.5	7.6 +/- 0.4
DM	% FM	31.2	25.3	28.6	28.4 +/- 3.0
VS	% DM	60.9	68.1	51.0	60.0 +/- 8.6
C_{org}	% DM	32.0	38.5	28.3	32.9 +/- 5.1
MP	Nl kg^{-1} VS	243	347	259	283 +/- 51

4.5 Conclusion

The results of this study emphasize that element retention in the digester system has a decisive impact on final element content in the digestate, especially for N, P and Mg. However, the comparison to other studies shows that the extent of element retention is depending on nutrient and heavy metal content of feedstock and process conditions during anaerobic treatment. Finally, results of this study

underline the influence of feedstock quality on final digestate characteristics. Therefore, ensuring MOW quality is seen as the crux for the successful utilization of digestates as soil amendments and for the closure of material and nutrient circles.

5 Effect of drying, composting and subsequent impurity removal by sieving on the properties of digestates from municipal organic waste

This chapter was published as: Knoop, C., Dornack, C., Raab, T., 2018. Effect of drying, composting and subsequent impurity removal by sieving on the properties of digestates from municipal organic waste. Waste Management 72, 168-177. doi: 10.1016/j.wasman.2017.11.022.

5.1 Abstract

The application of organic soil amendments is a common measure to prevent structural degradation of agricultural soils and to maintain and improve long-term soil fertility. Solid residues from anaerobic digestion of municipal organic waste (MOW) are rich in nutrients and organic matter and have a promising potential to be used as soil amendment. However, no study has related amendment properties of MOW digestate of one origin to different treatment procedures. We therefore investigated the impact of drying, composting and sieving on final digestate properties and specifically nutrient availability and heavy metal and carbon elution.

Samples were provided by a semi-industrial two-stage biogas plant with dry fermentation of MOW. Results confirm that in comparison to drying, composting of MOW digestates leads to a significant increase of K, P, Mg, Ca, Cd and Cr in the digestates. Sieving of composted digestates showed that heavy metals are not evenly distributed and that heavy metal concentration in the digestate increases with decreasing mesh sizes (highest concentrations in the fractions <1 mm). Although the element concentration is higher in composted batches, the water-extractability of nutrients, heavy metals and carbon is significantly lower from composted over dried digestates. A significant correlation was found between the dissolution of Zn, Ni, Ca and Mg and pH of eluate as well as dissolved organic carbon (DOC) release ($R > 0.7$, $p < 0.05$). Results confirm that the extent of carbon elution depends on the degradation rate of digestates. DOC may therefore be a good measure to evaluate digestate stability and to decide on treatment measures.

5.2 Introduction

One of the requirements of the EU Waste Framework Directive is that member states take measures to establish a separate collection of biowaste and to encourage the utilisation of materials produced from biowaste (Directive 2008/98/EC, Article 22). In Germany, every household has been obliged to collect organic waste in a separate bin since 2015 (Kreislaufwirtschaftsgesetz, KrWG, § 11). This facilitates a nationwide recovery of municipal organic waste (MOW), which refers to all kitchen and garden waste from private households. One possibility to recover the energetic potential of MOW is anaerobic digestion. In 2014, the total digestion capacity for organic waste was 1.9 million tons in more than 100 plants operating (Kern and Raussen, 2014). Along with the recent subsidies policy development under the German Renewable Energies Law (Erneuerbare-Energien-Gesetz, EEG) and the search for alternative, cost-efficient and sustainable biogas substrates an increase of MOW utilisation in biogas plants can be expected (Kern and Raussen, 2014; Schüch et al., 2016).

Anaerobic digestates have been investigated by a few studies (Al Seadi et al., 2013; Maynaud et al., 2017; Pognani et al., 2012; Risberg et al., 2017; Zirkler et al., 2014), which show that they provide a broad range of nutrients and residual organic compounds. Final digestate properties depend on feedstock composition, process conditions during digestion and post-treatment. Altogether, anaerobic digestates are considered as valuable fertilizer and humus source and shall therefore be redistributed to arable land as soil amendment (Alburquerque et al., 2012a; Insam et al., 2015; Nkoa, 2014). Digestate treatment aims to reduce the digestate mass, to guarantee hygienic and ecological harmlessness and to provide a storable, transportable, tradable and applicable fertilizer product of high quality. Legal requirements (nitrogen-limits, contamination thresholds) and economical aspects (limited storage capacity, high transportation costs) as well as limited application options (oversupply of fields, blocking periods) increase pressure on plant operators to adapt digestate management. Digestate treatment is becoming a substantial part of the successful operation of biogas plants (Dahlin et al., 2015).

There is a variety of treatment options for digestates (Al Seadi et al., 2013; Drosg et al., 2015). However, the treatment of solid digestates from MOW is challenging as they are subject to stricter legal requirements than digestates originating from agricultural crops. According to the German Fertilizer Ordinance (Düngemittelverordnung, DüMV) and the German Biowaste Ordinance (Bioabfallverordnung, BioAbfV) impurity and heavy metal content of digestates as well as hygiene are crucial quality criteria. Impurities such as plastics, metals or glass mainly result from miss-sorting during on-site collection. Total impurity content of the amendment must not exceed 0.5% of dry matter (§ 4, BioAbfV). 40% of German biogas plants utilising MOW operate with thermophilic temperature conditions (Fricke et al., 2014b). Hence, the predominant proportion of solid digestates does not fulfill hygiene criteria. Consequently, the removal of impurities and hygienisation are the main treatment objectives to obtain a high-quality amendment product. Hygienisation can be realised by composting or drying of digestates. Impurity removal is usually done by sieving.

The effect of these treatment steps on digestate properties will therefore be investigated in this study.

There have been a few investigations on fermentation residues application (Insam et al., 2015; Nkoa, 2014). However, most research focuses on characteristics and impact of untreated digestates (water content 95–98%) from wet fermentation of energy crops and manure on soil and plant development (Abubaker et al., 2013; Alburquerque et al., 2012b; Voelkner et al., 2015). There has also been research on the effect of application of solid residues from MOW digestion (Odlare et al., 2015; Odlare et al., 2011). However, no study related amendment properties of one digestate to different treatment procedures yet. We suppose that the application of MOW digestates affects nutrient, heavy metal and carbon availability in soil and that the way of digestate treatment influences soil performance of final amendment products. This study therefore aims to investigate and compare the properties of MOW digestates of one origin after drying or composting and sieving under laboratory and semi-industrial scale conditions and to evaluate the potential impact of treated MOW digestates on available nutrients, heavy metals and carbon in the soil solution. The results obtained shall deliver new insights into the impact of MOW digestates on soil and contribute to a better understanding of how digestate treatment influences the quality of soil amendments.

5.3 Materials and methods

5.3.1 Origin of digestates, post-treatment and sampling

Three batches of digestates (D1, D2, D3) were obtained from a semi-industrial scale two-stage biogas plant using MOW as feedstock (see Table 8 for sample acronyms). MOW was separately collected and provided by a local composting facility from a small town near Dresden (Saxonia, Germany). MOW collection and subsequent test series took place from May to July 2016. An overview of MOW and digestate treatment is presented in Figure 8. Prior to digestion, MOW

was mixed with organic bulk material. Feedstock was treated in a semi-industrial scale two-stage biogas plant consisting of two anaerobic hydrolysis box fermenters (40 m^3), an anaerobic fixed-bed digester (14 m^3) and two percolate storage tanks. Hydrolysis digesters were operated in batch under continuous percolation with process liquid. Percolate was subsequently fed to the fixed-bed digester (carrier media: RVT-Bioflow 401) for methanation. Process temperature in the digesters was 37–40 °C. Retention time of MOW in the hydrolysis box fermenters was 14 days. At the end of the digestion process percolation was stopped and digestate was drained. Process liquid remained in the storage tanks of the biogas plant.

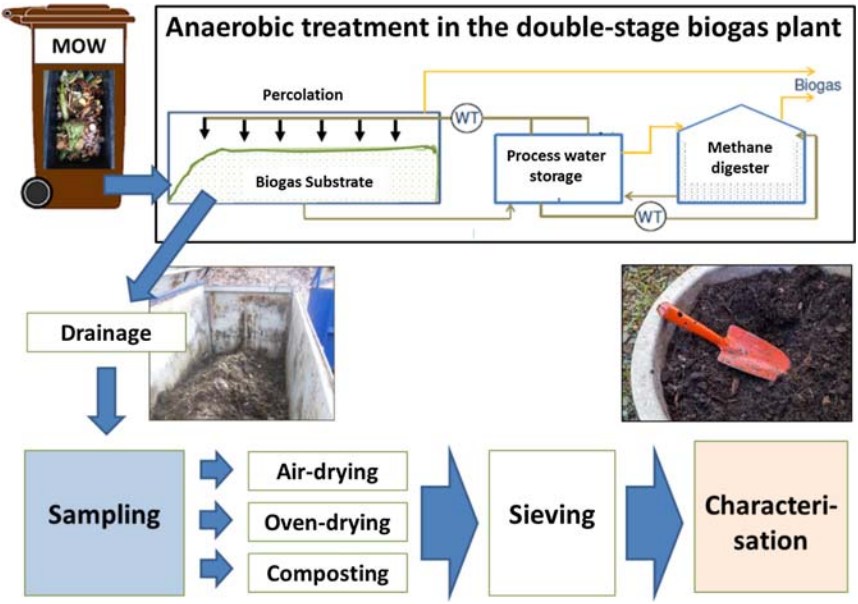

Figure 8: Overview of MOW and digestate treatment during the experiments

Solid digestate was removed from the hydrolysis fermenters and a composite sample of 50 kg was taken for drying. The remaining digestate was delivered to a composting plant near Dresden (Saxonia, Germany), where it was treated in open heaps for 6 weeks ($D1_{comp}$, $D2_{comp}$, $D3_{comp}$). Drying was carried out within our laboratory facilities. 25 kg of each batch were dried at 70 °C in a laboratory oven ($D1_{oven}$, $D2_{oven}$, $D3_{oven}$). Another 25 kg were air-dried at 20–30 °C ($D1_{air}$, $D2_{air}$, $D3_{air}$). The drying process was finished when the weight of digestate remained constant.

All digestates were manually sieved at a mesh size of 20 mm to remove bulk material and impurities. A composite sample of 2 kg of fresh matter (FM) was taken from all dried and composted samples of every batch. ½ of the sample was stored in the freezer. The rest was dried at 105 °C, impurities >2 mm were removed and the leftover sample was shredded in a laboratory cutting mill and subsequently ground in a mortar mill until a particle size of 0.25 mm was reached.

5.3.2 Determination of digestate characteristics

Fresh samples were used to determine pH, plant available nitrogen (N_{pa}), plant available phosphorus (P_{pa}), plant available potassium (K_{pa}) and salt content according to the analysis handbook of German Federal Compost Association (BGK, 2006). pH and N_{pa} were measured after 1 hour extraction of a 20 g sample (DM) with 200 ml $CaCl_2$ solution using a WTW pH meter (inoLab Multi 9620) and a Shimadzu TN/TOC-Vcph-Analyzer (N_{pa}). P_{pa} and K_{pa} were quantified after 1 hour extraction of a 20 g sample (DM) with 200 ml calcium-lactate-acetate solution with ICP-OES. Salt content was determined after 1 hour extraction of a 20 g sample (DM) in 200 ml deionized water with WTW meter (inoLab Multi 9620). All extractions were examined on a shaker at 100 rpm and extracts were filtered before measurement (Whatman cellulose filter N°1). Water content or dry matter (DM) content of fresh samples was quantified after 24 hours drying at 105 °C (DIN EN 13040).

The dry and ground sample was used for the quantification of volatile solids (VS), total carbon (C), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn) and cation exchange capacity (CEC). VS was determined after 3 hours ignition of a 3 g sample (DM) at 550 C in a muffle furnace (DIN EN 12879). C and N were measured after combustion of a 2 mg sample (DM) in an automatic CNS-Analyser (Vario EL III, DIN ISO 10694). P, K, Ca, Mg, Cd, Cr, Cu, Ni, Zn and Pb were determined after pressure digestion of a 0.3 mg sample (DM) in aqua regia (DIN EN 13567) with ICP-OES (DIN EN ISO 11885). CEC was quantified by shaking a 5 g sample (DM) with 30 ml $BaCl_2$ solution (3 times, 100 rpm) and applying $MgSO_4$ solution (once, 100 rpm) to fill free exchange places (DIN 19684-8). After the experiment, Mg in the solution was determined with ICP-OES.

All analyses were carried out in duplicate. All sample values investigated refer to the dry matter (DM).

Table 8: Overview of acronyms used for sample description

Acronym	Meaning
MOW	Municipal Organic Waste
D	Digestate
D_{fresh}	Fresh digestate
D_{air}	Air-dried digestate
D_{oven}	Oven-dried digestate
D_{comp}	Composted digestate
DM	Dry matter
FM	Fresh matter
HM	Heavy metals
pa	plant available

5.3.3 Determination of nutrient, heavy metal and carbon elution from digestates

Elution potential of digestates was determined according to DIN EN 12457-4. Fresh samples of dried and composted digestates were used. The test was carried out in quadruplicate. Input of each flask was 90 g DM. It was mixed with deionized water at a ratio of 1:10 and shaken for 24 hours at 50 rpm. Eluate was centrifuged at 18,500g for 10 minutes and filtered twice (first: Whatman cellulose filter N°1, second: Macherey-Nagel syringe filter 0.45 µm). Nutrient contents (P, K, Mg and Ca) as well as heavy metals concentrations (Cd, Cr, Cu, Ni, Pb, Zn) in the eluate were determined with ICP-OES. Dissolved organic carbon (DOC) in the eluate was quantified with a Shimadzu TN/TOC-Vcph-Analyzer.

5.3.4 Determination of heavy metal distribution in the fine fraction (<20 mm) of composted digestates

Based on the findings about high heavy metal contents in the digestates D1–D3, it was decided to investigate the distribution of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) within the fine fraction (<20 mm) of composted digestates. Therefore, composite samples of another three batches of digestates (D4, D5, D6) were taken after treatment at the composting plant (treatment as explained in Section 2.1). Sample size was 40–50 kg of each composted and sieved batch. Each sample was manually sieved at mesh sizes 10 mm and 5 mm. Each fraction (10–20 mm, 5–10 mm, <5 mm) was weighed and a sample was taken for dry matter determination after 24 hours drying at 105 °C (DIN EN 13040). Another 700 g of the fraction <5 mm was taken for subsequent wet sieving using mesh sizes 2 mm, 1 mm and 0.5 mm. The sample was continuously rinsed with water during wet sieving. Dry weight of resulting fractions was again determined after 24 hours drying at 105 °C (DIN EN 13040). Dried samples were ground in a mortar mill to a particle size of 0.25 mm and heavy metal analysis was conducted according to DIN EN 13567 and DIN EN ISO 11885 (see Section 5.3.2). Mass balance was done referring to the dry weight of all fractions.

Total heavy metal content (HM_{abs}) of each sieve fraction and for each element was calculated with the following equation:

$$HM_{abs} = DM_{abs} * HM_c$$

Equation 6: Heavy metal content (HM_{abs} in mg), DM_{abs} = dry weight of fraction after sieving in kg, HM_c = measured heavy metal concentration in mg kg $^{-1}$

5.3.5 Evaluation of analysis results

Raw data was checked for normal distribution by Kolmogorov-Smirnov-test and for outliers by Dixon's Q test, which are both suitable for small sample sizes. Significance of differences between means of data was tested by one-way ANOVA followed by Tukey test.

Table 9: Characteristics of dried and composted digestates of batches D1-3 (DM = dry matter, FM = fresh matter, VS = volatile solids, PSU = Practical Salinity Units)

		Dried digestate				Composted digestate			
		D1	D2	D3	**Mean**	$D1_{comp}$	$D2_{comp}$	$D3_{comp}$	**Mean**
Nutrient content									
N		20.6	18.8	21.9	**20.4 +/- 1.6**	19.8	24.8	23.4	**22.7 +/-2.8**
P		3.9	3.1	3.8	**3.6 +/- 0.4**	4.3	4.5	4.5	**4.4 +/- 0.1**
K	g kg^{-1} DM	7.5	6.9	10.7	**8.4 +/- 2.0**	10.8	10.8	10.9	**10.8 +/- 0.1**
Mg		4.1	4.8	3.9	**4.3 +/- 0.4**	5.6	5.7	5.3	**5.6 +/- 0.2**
Ca		23.0	25.1	23.9	**24.0 +/- 1.0**	30.1	29.5	30.1	**29.9 +/- 0.4**
Heavy metal content									
Cd		2.2	2.5	1.9	**2.2 +/- 0.3**	3.1	3.3	3.4	**3.3 +/- 0.2**
Cr		26.6	34.0	24.4	**28.3 +/- 5.0**	36.1	60.6	55.6	**50.8 +/- 13.0**
Cu	mg kg^{-1} DM	90.9	80.0	67.5	**79.5 +/- 11.7**	74.8	113.8	80.2	**89.6 +/- 21.1**
Ni		12.4	17.7	9.8	**13.3 +/- 4.0**	15.0	30.3	13.5	**19.6 +/- 9.3**
Pb		268.3	345.0	192.8	**268.7 +/- 76.1**	334.0	355.5	297.9	**329.1 +/- 29.1**
Zn		540.5	635.9	-	**588.2 +/- 67.5**	574.1	732.5	548.9	**618.5 +/- 99.5**
Further parameters									
DM D_{fresh}		33.7	29.8	32.7	**32.1 +/- 2.0**				
DM D_{air}	% FM	98.2	95.9	97.4	**97.2 +/- 1.1**	50.6	48.8	51.5	**50.3 +/- 1.4**
DM D_{oven}		99.1	99.1	99.2	**99.1 +/- 0.0**				
VS	% TM	53.8	53.8	56.1	**54.5 +/- 1.3**	43.5	43.5	45.2	**44.1 +/- 1.0**
C	% TM	31.0	29.7	34.6	**31.8 +/- 2.5**	21.8	25.8	25.8	**24.4 +/- 2.3**
pH D_{fresh}		6.0	6.1	6.8	**6.3 +/- 0.4**				
pH D_{air}		6.3	6.1	6.3	**6.2 +/- 0.1**	7.1	7.2	7.3	**7.2 +/- 0.1**
pH D_{oven}		5.8	5.6	6.4	**6.0 +/- 0.4**				
Salt content D_{fresh}		0.4	0.3	0.4	**0.4 +/- 0.1**				
Salt content D_{air}	PSU	1.1	1.2	1.0	**1.1 +/- 0.1**	0.1	0.1	0.2	**0.1 +/- 0.1**
Salt content D_{oven}		1.3	0.8	1.0	**1.1 +/- 0.2**				

5.4 Results

5.4.1 Properties of dried and composted digestates

The investigation on substrate properties after drying and composting revealed clear differences between treated digestates (Table 9). On average, the total nutrient concentration in composted digestates (D_{comp}) is 20–30% higher than in dried digestates (D_{air}, D_{oven}) (except for N), caused by organic matter degradation and microbial conversion processes during composting. Significantly higher contents were found for P, K, Mg and Ca. The content of heavy metals also increases during composting. This is significant for Cd and Cr. Highest increase was determined for Cr, Cd and Ni (50–80%). However, the results of heavy metal analysis also show a high variance between the three batches as expressed by high standard deviations.

Table 10: Plant available N, P and K as well as CEC of dried (oven-dried at 70°C, air-dried at 20-30°C) and composted digestates of batches D1-3 (DM = dry matter, pa = plant available)

	fresh	air-dried	oven-dried	composted
N_{pa} [g kg^{-1} DM]	3.7 +/- 0.4	1.3 +/- 0.5	1.2 +/- 0.3	0.6 +/- 0.2
N_{pa} [% of N_{total}]	15.5 +/- 1.9	5.9 +/- 2.6	5.4 +/- 1.2	2.6 +/- 0.4
P_{pa} [g kg^{-1} DM]	1.0 +/- 0.2	0.7 +/- 0.1	0.7 +/- 0.2	1.2 +/- 0.1
P_{pa} [% of P_{total}]	29.1 +/- 7.1	20.5 +/- 5.6	20.8 +/- 4.5	27.5+/- 1.7
K_{pa} [g kg^{-1} DM]	5.8 +/- 0.3	5.0 +/- 0.6	5.4 +/- 0.8	6.0 +/-0.7
K_{pa} [% of K_{total}]	69.1 +/- 11.5	62.7 +/- 4.3	66.0 +/- 6.8	54.4 +/- 6.2
CEC [cmol kg^{-1} DM]	-	22.0 +/- 1.6	23.6 +/- 0.4	28.9 +/- 1.3

The DM content of digestates is highest for oven-dried batches (99% FM) followed by air-dried (97% FM), composted (50% FM) and fresh digestates (32% FM). The content of VS is reduced from 55% to 44% by digestate composting. Average total C content of digestates is decreased by 23% during composting.

Furthermore, composting of digestates leads to an elevation of pH from 6.3 to 7.2. Drying does not significantly change the pH of digestates. Salt content of fresh digestates (0.4) is increased by drying (1.1) and lowered by composting (0.1).

The results obtained for plant available nutrients are presented in Table 10. Fresh digestates contain the highest share (15% of total N) of plant available N (N_{pa}). The results of N_{pa} analysis are similar for air-dried and oven-dried digestates (5–6% of total N). N_{pa} of dried digestates accounts for about one third of N_{pa} of fresh digestates. Lowest N_{pa} values have been determined for composted digestates (2–3% of total N). This shows that the loss of N_{pa} is highest during composting (84%) and significantly lower during air-drying (66%) and oven-drying (68%).

Plant available P (P_{pa}) is highest in composted digestates, but does not significantly differ from fresh digestates. Up to 30% of total P is plant available in the investigated fresh and composted digestates. P_{pa} obtained for dried digestates is significantly lower averaging at 21% of total P. There is no significant difference between digestates for plant available K (K_{pa}). Up to 70% of total K in the investigated digestates can be found in the eluate and are therefore considered as plant available. CEC is significantly higher in composted digestates (29 cmol kg^{-1} DM) than in dried digestates.

5.4.2 Nutrient, heavy metal and carbon elution from dried and composted digestates

The results of the elution experiment revealed a considerably higher water extractability of nutrients from dried digestates than from composted digestates (Figure 9).

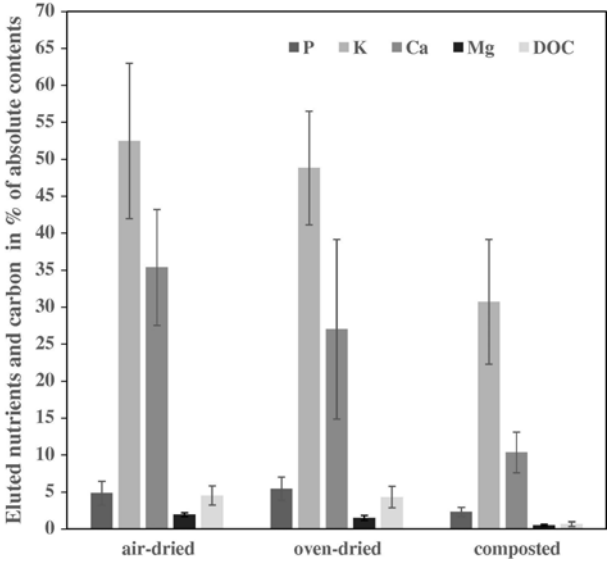

Figure 9: Nutrient elution from dried and composted digestates of batches D1-3

Differences of nutrient elution between air-dried and oven-dried digestates are not significant according to Tukey test. Water-soluble P accounts for 5% of total P contained in the dried digestate and 2% of total P contained in the composted digestate. The amount of eluted K during the 24-hours-experiment averages at 52% of total K in the air-dried, 49% in the oven-dried digestates and only 31% in the composted batches. 2% of total Mg contained in the sample are eluted from dried digestates, which is in contrast to 0.5% of total Mg eluted from composted digestates. The same effect was detected for Ca with 27% and 35% eluted from dried samples and 10% eluted from composted ones. Summing up all nutrients

determined, elution from composted digestates accounts only for 54% of nutrients eluted from the dried batches.

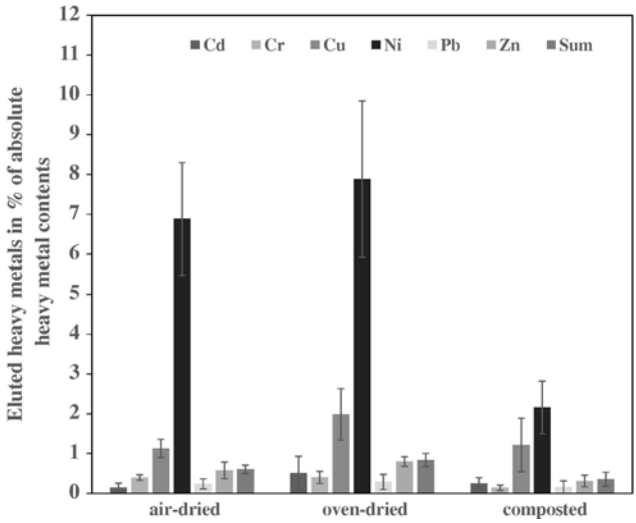

Figure 10: Heavy metal elution from dried and composted digestates of batches D1-3

Heavy metal elution is also higher from dried digestates than from composted digestates (Figure 10). According to Tukey test a significant difference can be found between investigated batches for the elution of Cr, Ni and Zn. Ni elution is highest in all samples. In the dried digestates, water-soluble Ni sums up to 8% of total Ni content in the sample. In comparison, Ni eluted from composted digestates accounts only for 2% of total Ni content. Altogether, the elution of heavy metals is below 1% of total heavy metal content in all batches.

The elution of dissolved organic carbon (DOC) from the treated digestates is clearly lowest from the composted samples (Figure 9). DOC accounts for up to 5% of total C contained in the dried samples and below 1% in the composted ones. Again, air-dried and oven-dried samples do not differ distinctly. Linear regression analysis revealed a very strong, negative correlation between pH of eluate and DOC ($R = -0.98$, $p < 0.05$) (Figure 11). Furthermore, a significant positive correlation ($p < 0.05$) was found between the concentration of DOC and

Mg (R = 0.92), Ca (R = 0.90), Ni (R = 0.75) and Zn (R = 0.82) in the eluate (Table 11).

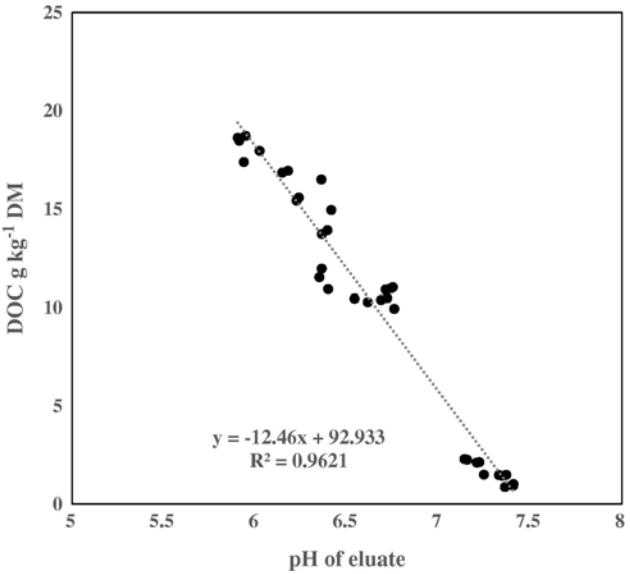

Figure 11: Carbon elution from dried and composted digestates of batches D1-3 in function of pH in the eluate

Table 11: Results of linear regression analysis for eluted elements in function of pH (R_{pH}) and DOC (R_{DOC}) in the eluate (Correlations > 0.7 are highlighted, p < 0.05)

	R_{pH}	R_{DOC}
P	-0.30	0.35
K	-0.16	0.27
Mg	**-0.85**	**0.92**
Ca	**-0.84**	**0.90**
Cd	0.06	-0.10
Cr	-0.44	0.48
Cu	-0.32	0.23
Ni	**-0.75**	**0.75**
Pb	-0.17	0.16
Zn	**-0.87**	**0.82**
DOC	**-0.98**	1.00

5.4.3 Heavy metal distribution in composted digestates

The fractionation of post-treated digestates $D4_{comp}$–$D6_{comp}$ (particle size <20 mm) shows that heavy metals are not evenly distributed in the samples (Figure 12). 80% of total heavy metal load in the composted digestate can be found in the fraction smaller than 10 mm, 55% in the fraction smaller than 5 mm and 35% in the fraction smaller than 2 mm. Highest analysis results were determined in the composted digestates for Zn and Pb (Table 12). Thresholds of German Biowaste Ordinance are exceeded for Cd and Zn in $D4_{comp}$ and $D5_{comp}$. Heavy metal concentration reaches maxima in the fractions smaller than 1 mm (Figure 13). This is significant for the elements Cd and Ni. It indicates that sieving leads to an accumulation of heavy metals in the composted digestates. The smaller the applied mesh size, the higher is the heavy metal concentration in the composted digestate.

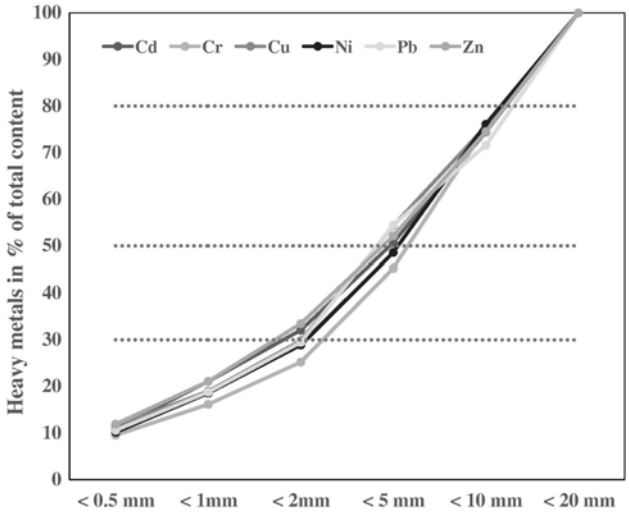

Figure 12: Distribution of heavy metals in the composted digestate (fraction < 20 mm) of batches D_{comp}4-6

5.5 Discussion

5.5.1 Nutrient provision of digestates

Results of our experiments show that there are significant differences in the amendment properties of dried and composted digestates. Total nutrient and heavy metal content of composted digestates is higher than of dried digestates of one batch. This is caused by the degradation of organic matter during composting, which leads to further accumulation of elements in the digestate and to microbial conversion of solid remains (Maynaud et al., 2017; Pognani et al., 2012). Additionally, higher structural complexity of residual organic matter in the composted digestates may enhance nutrient bonding, which subsequently leads to higher nutrient enrichment in the solid residue. With regard to digestate utilisation this means that, if the application of amendments produced from MOW is limited by the dry matter as in Germany (§ 6, BioAbfV), the total nutrient and heavy metal supply to soil is higher when using composted over dried digestates.

Table 12: Heavy metal concentration in composted batches D_{comp}4-6 (< 20 mm)

Heavy metal content of composted digestates (D4-D5)		**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
				in mg kg^{-1} DM			
$D4_{comp}$		2.2	42.6	63.2	22.9	141.6	442.7
$D5_{comp}$	**< 20 mm**	2.9	27.0	97.2	22.3	140.4	510.2
$D6_{comp}$		0.7	27.9	49.7	15.5	112.9	344.6

The comparison of results on nutrient contents with existing literature shows that the determined N, P, Mg and Ca concentration in dried digestates is lower than found in other studies on digestates from organic waste (Lorenz et al., 2014; Stoknes et al., 2016; Tampio et al., 2016). Total K content of digestate samples is in line with the findings of Lorenz et al. (2014) and Stoknes et al. (2016). In contrast, total contents of N, P, K and Mg of composted digestates investigated are higher than the results determined during a study on compost quality in

German treatment plants by the German Federal Compost Association (BGK, 2016). This is also the case for mean N and K but not for P contents found by a review on composts worldwide by Faverial et al. (2016). In contrast, Stoknes et al. (2016) report higher contents of N and P in vermicompost produced from food waste digestates. The research for results on digestates and composts from other studies reveals a great variability of data. Composition and treatment of feedstocks are the major influence factors for digestate and compost properties (Al Seadi et al., 2013; Bilitewski and Härdtle, 2013; Faverial et al., 2016; Knoop et al., 2017; Risberg et al., 2017; Zirkler et al., 2014). Deviations of nutrient contents of dried and composted digestates between this and other studies may therefore be caused by the variability and nutrient provision of feedstocks as well as the process parameters during digestion and the rate of substrate degradation.

In this study, highest share of plant available (pa) N was found in the fresh digestate. Dried digestates contain about one third of N_{pa} of fresh digestates. Lowest N_{pa} values have been determined for composted digestates showing that the loss of N_{pa} is highest during composting. These results are confirmed by other studies revealing a significant higher N_{pa} content in fresh digestates (Lorenz et al., 2014) than in composts (BGK, 2016; Drosg et al., 2015; Stoknes et al., 2016). Plant available P is highest in composted digestates, but does not significantly differ from fresh digestates. Up to 30% of total P is plant available in fresh and composted digestates investigated. P_{pa} obtained for dried digestates is considerably lower averaging at 21% of total P. BGK (2016) and Stoknes et al. (2016) reinforce the high plant availability of P in composts (43% and 54% of total P). Unlike the results obtained in this study the differences in the share of plant available P between fresh and composted digestates seem to be more significant in the study of Stoknes et al. (2016), which may however be caused by higher total P contents in the digestate. No clear difference for plant available K was found between digestate samples investigated. The same is confirmed by other studies (BGK, 2016; Stoknes et al., 2016). Up to 70% of total K can be considered as plant available in the investigated samples. The plant availability of K can even be up to 90% (Stoknes et al., 2016) and does not seem to be influenced

by digestate treatment. Cation exchange capacity (CEC) controls a substrates ability to absorb specific cations such as Ca^{2+}, Mg^{2+}, K^{+} and Na^{2+}. Our results show that CEC is significantly higher in composted digestates than in dried digestates. According to Teglia et al. (2011b) CEC depends on the degradation rate of feedstocks and rises during biological treatment. It can therefore be concluded, that composted digestates have a higher contribution to enhance the CEC of soil. This is confirmed by a study of Leinweber et al. (1993) proving that CEC was highest in soils amended with compost compared to manure or straw amendments.

5.5.2 Heavy metal contents in digestates

Heavy metal contents in digestates and composts have been investigated by several authors (BGK, 2016; Govasmark et al., 2011; Kupper et al., 2014; Smith, 2009; Stoknes et al., 2016). In comparison to these studies, the total heavy metal contents in our experiments are significantly higher for Cd, Pb and Zn in all samples. Cr, Cu and Ni concentrations of digestates are in line with the findings of Stoknes et al. (2016), German Federal Compost Association (BGK, 2016) and Kupper et al. (2014). Cr, Cu and Ni values in composted digestates investigated are also slightly higher than results gained in other studies (BGK, 2016; Govasmark et al., 2011; Kupper et al., 2014). However, due to high standard deviations, differences are not significant. The cause for a higher Cd, Pb and Zn contamination of samples of this study is presumed in a high initial heavy metal load of feedstocks (values determined in mg kg^{-1}: Cd = 2.1, Cr = 24.8, Cu = 53.5, Ni = 11.0, Pb = 225.5, Zn = 422.7). Additionally, anaerobic digestion and subsequent composting result in heavy metal accumulation due to degradation of organic compounds. Consequently, in this study the heavy metal concentration in the dried digestates is lower than in the composted digestates. This is underlined by the findings of Kupper et al. (2014).

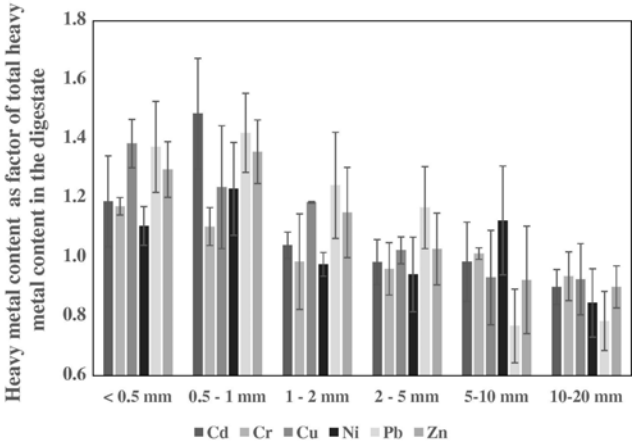

Figure 13: Heavy metal content in sieve fractions of batches D_{comp}4-6 (content of each sieve fraction is expressed as factor of total heavy metal content in the digestate as presented in table 12)

Both digestates and composted digestates in our trials exceed legal thresholds of German Biowaste Ordinance (BioabfV, §4) for Cd, Pb and Zn. They would therefore not be suitable as soil amendments. This emphasizes the importance of feedstock quality. There are different sources for heavy metal contamination of feedstocks. Impurities highly contribute to heavy metal concentration (Amlinger et al., 2004; Kupper et al., 2014; Rotter, 2002; Smith, 2009). Batteries, metals and electronic scrap as well as ink from newspapers contain heavy metals (Smith, 2009). In this study, the impurity content in the feedstocks reaches up to 10%. As no impurities and metal removal was conducted as pretreatment this can be seen as one reason for high heavy metal contents of investigated samples. Another important source for heavy metals are fine particles such as soil and dust contained in hoover bags, road sweepings and gardening waste (Smith, 2009; Veeken and Hamelers, 2002). Furthermore, feedstocks investigated may contain higher heavy metal contents due to geological background exposure. A heavy metal contamination of digestate during sieving and shredding in our lab cannot be fully excluded as stainless steel blades and meshes were used. However, we expect that this effect is rather low, as investigations with non-contaminated

samples have not been conspicuous. Investigations by Kupper et al. (2014) show that heavy metal contamination of feedstocks seem to occur at random. However, these contamination hot spots decrease overall feedstock and subsequently digestate quality. To improve feedstock quality on-site separation of waste needs to be conducted with high responsibility.

5.5.3 Influence of organic stability on digestate properties

Organic matter degradation during composting treatment causes differences between properties of dried and composted digestates. Whereas drying leads to conservation of the current state of digestates, composting results in changes of substrate properties caused by conversion processes during composting. The content of volatile solids and carbon is decreased by composting due to aerobic decomposition of organic compounds to CO_2, H_2O and heat. This is confirmed by the findings of Maynaud et al. (2017), which show that composting of digestates significantly reduces biodegradable organic matter content and that the remaining organic matter contains less accessible compounds of higher structural complexity. pH of digestates is rising towards neutral during composting, which is also a typical sign for the completion of degradation processes and a good biological substrate stability (Bilitewski and Härdtle, 2013). Salt content of investigated digestates decreases during composting, which is probably caused by leaching of process liquid as open heaps are exposed to rainfall.

Our results prove that water dissolution of nutrients from dried digestates is double as high as from composted batches. The release rate differs for each element and has the following order: K > Ca > P > Mg. During a rainfall simulation experiment with compost Al-Bataina et al. (2016) found that nutrient elution depends on compost age or rather on the degradation rate of organic matter. The elution of N, P and DOC decreased with increasing compost age. Contrary to that, the elution of K increased with increasing compost age (Al-Bataina et al., 2016), which is however not reflected by the data of this study. During investigations on P availability Wei et al. (2015) discovered that water-

soluble P in the organic waste substrates decreased with progress of the composting process. One reason for higher nutrient release from dried digestates may therefore be its lower rate of degradation. It can be assumed that the residual organic matter in the dried digestates has a lower structural complexity than in the composted digestates. Maynaud et al. (2017) confirmed by 3D fluorescence spectroscopy of organic matter extracts that the stability of organic compounds in the digestate depends on the applied post-treatment. Solid digestates without composting post-treatment contained a larger part of easily accessible and less complex forms of molecules. The binding strength of nutrient ions may therefore be lower, resulting in a higher elution potential of dried digestates. Similar results can be found regarding the release of heavy metals during our experiment. Again, elution is higher from dried digestates than from composted digestates. A significant difference between investigated batches was found for Cr, Ni and Zn. Ni was eluted best (up to 8% from dried digestates, 2% from composted digestates). According to Blume et al. (2016) the bonds between Cd, Zn or Ni ions and absorbent are less strong in comparison to other heavy metals, which results in a higher release potential. In total, the dissolution of heavy metals is below 1% of total heavy metal content in all batches. The release of heavy metals from organic amendments has been studied by several authors (Antoniadis and Alloway, 2002; Cambier et al., 2014; Fang et al., 2017). Additionally, knowledge on heavy metal dynamics in the soil solution can be retrieved from aquatic chemistry (Stumm and Morgan, 1996) and wastewater treatment (Ali et al., 2012b; Christensen et al., 1996; Khokhotva and Waara, 2010; Kunhikrishnan et al., 2017). Summarizing the findings from literature, the mobility of heavy metals is highly dependent on the availability of DOC. DOC is comprised of organic molecules below 0.45 µm, resulting from decomposition processes of organic matter. It contains functional surface groups (Stumm and Morgan, 1996), which are able to absorb heavy metal ions by forming soluble organo-metal complexes and therefore have an important influence on heavy metal availability (Christensen et al., 1996; Kunhikrishnan et al., 2017). It was also reported that

DOC is competing more effectively for free metal ions (Khokhotva and Waara, 2010) and reduces metal adsorption in the soil (Antoniadis and Alloway, 2002).

The amount of water-extractable carbon depends on the rate of mineralization of organic compounds (Said-Pullicino et al., 2007). The elution of carbon from investigated digestates is significantly lowest from the composted samples (1% of total C). DOC accounts for up to 5% of total C contained in the dried samples. This indicates that organic compounds in composted digestates are more stable, which in turn results in a lower water-solubility as reported by Said-Pullicino et al. (2007). A high DOC concentration in the soil solution promotes heavy metal uptake by plants. During a pot experiment, uptake of Ni and Zn by ryegrass was significantly higher in pots with higher DOC concentrations (Antoniadis and Alloway, 2002). A similar result was obtained by Christensen et al. (1996) during investigations on landfill leachate. Cd, Ni and Zn preferentially bond to DOC, clearly indicating a complexation. Fang et al. (2017) determined increased leaching of Cd, Cr, Cu, Ni and Pb with increasing DOC in the soil solution during a percolation experiment with sewage sludge. Results from these studies underline our findings from linear regression analysis which revealed a significant positive correlation ($p < 0.05$) between carbon elution and the elution of Ni ($R = 0.75$) and Zn ($R = 0.82$) from the digestate. The same effect is assumed for Mg ($R = 0.92$) and Ca ($R = 0.90$). Furthermore, results show that carbon elution is higher from dried digestates with low pH ($R = -0.98$, $p < 0.05$). A low pH favours the solubility of heavy metals, because negative surface charges of heavy metal adsorbing compounds are reduced by the adsorption of H ions (Ali et al., 2012b; Blume et al., 2016). The pH difference resulting from the different treatments may therefore be another reason for a higher heavy metal availability of dried digestates. Furthermore, (Christensen and Christensen (2000) found that the binding of Cd, Ni and Zn to DOC is most effective at pH 5–7, which is within the pH range of dried digestates investigated.

The elution of carbon is also known as criterion for the maturity of composts and reaches steady-state towards the end of the composting process (Zmora-Nahum

et al., 2005). According to Said-Pullicino et al. (2007) a high carbon elution indicates unstable and immature waste. Shao et al. (2009) and Zmora-Nahum et al. (2005) found that DOC accounts for <5 g kg^{-1} of DM at the end of the composting process. Eluate of dried digestates of this study is characterised by a DOC of 14 g kg^{-1} of DM, whereas composted digestates cause a DOC of 1.5 g kg^{-1} of DM. This clearly indicates the difference in the stability of the organic matter between different digestate samples. To keep the dissolution of organo-metal compounds into soil solution low, Maynaud et al. (2017) recommend to only apply soil conditioners with high degradation stability. Zmora-Nahum et al. (2005) even demonstrated in a pot experiment with composts of different maturity that a high amount of DOC in the soil solution has a negative effect on plant growth.

5.5.4 Distribution of heavy metals in composted MOW digestates

Sieving of composted digestates is an essential treatment step to remove impurities from MOW digestates and to reach the impurity threshold value of <0.5% of DM required by the German Biowaste Ordinance (BioabfV, §4). Investigations on sieve fractions of composted digestates show that heavy metal content increases with decreasing particle size and that heavy metals are therefore not evenly distributed among the sieve fractions. About 80% of total heavy metal load in the treated digestate can be found in the fraction below 10 mm. Heavy metal concentration is highest in the sieve fractions below 1 mm. This is significant for the elements Cd and Ni. Our results underline findings of Smith (2009), Kupper et al. (2014) and Veeken and Hamelers (2002) who state that a considerable source for heavy metal contamination can be soil and dust particles. Additionally, the pretreatment, digestion and subsequent composting of MOW lead to particle size reduction and further distribution of impurities. Furthermore, a share of heavy metals may be dissolved during degradation and bond to fine particulate matter or precipitate as metal sulfides (Möller and Müller, 2012), which will subsequently be found in the fine fraction of digestates. Highest heavy metal contents in the composted digestates have been determined

for Zn and Pb. Two digestate samples exceed thresholds of German Biowaste Ordinance (BioAbfV, §4) for Cd and Zn caused by high feedstock contamination. From the results obtained, it can be concluded, that sieving leads to an accumulation of heavy metals in the composted digestates. The smaller the mesh size applied during sieving, the higher is the heavy metal concentration in the remaining composted digestate, as fractions of lower heavy metal contamination are removed with the sieve overflow. The removal of impurities is limited. There is no suitable solution for heavy metal removal. Additionally, organic matter degradation during treatment leads to accumulation of unwanted substances. This again puts the focus on improving the quality of feedstocks by responsible on-site separation. In a recent position paper of the German Federal Compost Association Kehres (2016) states that the impurity content of MOW should be below 1% of DM to enable the production of high quality soil amendments. Otherwise, treatment costs exceed benefits. However, it needs to be kept in mind that the German requirements for biowaste recycling on arable land are well advanced and that especially developing countries have only just begun to raise awareness for environmental issues of waste management and establish concepts for organic waste utilisation (Ali et al., 2012a; Surendra et al., 2014; Tock and Schummer, 2017). Still, improving feedstock quality is the most important measure to ensure sufficient final amendment quality and to enable the redistribution of MOW to the environment without harm (Al Seadi et al., 2013). Impurity removal by manual sorting in advance of the digestion process is most effective to prevent spreading of impurities and heavy metals in the digestate (Kehres, 2016).

5.6 Conclusion

Results of this study confirm that in comparison to drying, composting of solid digestates leads to accumulation of nutrients (significant for K, P, Mg and Ca) and heavy metals (significant for Cd and Cr) in the digestate. This is caused by organic matter degradation as indicated by a significant decrease of VS and C

during composting. Sieving of composted digestates investigated showed that heavy metals are not evenly distributed and that heavy metal concentration in the digestate increases with decreasing mesh sizes. Highest heavy metal concentration was found in the fractions below 1 mm. However, investigations also revealed a high variance of heavy metal contents between different MOW batches, which underlines the assumption that heavy metal loads occur randomly depending on feedstock contamination.

Although the element concentration is higher in composted batches, the water-extractability of nutrients, heavy metals and carbon is significantly lower from composted over dried digestates during our investigations. It is therefore assumed that for the short-term dried digestates have a greater impact on the chemical composition of soil solution than composted digestates. A significant correlation was found between the dissolution of Zn, Ni, Ca and Mg and pH of eluate as well as DOC release ($R > 0.7$, $p < 0.05$). Results confirm that the extent of carbon elution depends on the degradation rate of digestates. Therefore, organic matter stability seems to be a key factor regarding the potential performance of digestates in soil. The DOC content in the eluate may be a good measure to evaluate digestate quality and to decide on treatment measures.

Results indicate that heavy metal content of digestates caused by high heavy metal preload of feedstock and heavy metal redistribution during digestion and post-treatment can become a disadvantage with regard to region-specific heavy metal thresholds for soil amendments. Therefore, a low feedstock contamination is essential for the production of high quality amendments. Water extractability of heavy metals is significantly higher from dried over composted batches for Cr, Ni and Zn, which shows that low degradation stability increases heavy metal availability in soil. Altogether, composting seems to be a good option for the post-treatment of solid digestates with low organic matter stability.

6 Fate of nutrients and heavy metals during two-stage digestion and aerobic post-treatment of municipal organic waste

This chapter was published as: Knoop, C., Tietze, M., Dornack, C., Raab, T., 2018. Fate of nutrients and heavy metals during two-stage digestion and aerobic post-treatment of municipal organic waste. Bioresource Technology 251, 238-248. doi: 10.1016/j.biortech.2017.12.019.

6.1 Abstract

The biogas technology is a promising approach for the recovery of energy and fertilizer from municipal organic waste (MOW). However, only scarce information on the development of initial nutrient and heavy metal loads during processing is available. Therefore, this study investigates properties of source-separated MOW during treatment in a semi-industrial scale two-stage biogas plant and subsequent digestate composting including impurities removal. Data from 15 batch experiments was investigated by material and substance flow analysis. Results of this study have shown that about 40% of nutrients contained in the MOW inflow are mineralized during anaerobic and subsequent aerobic treatment. A higher nutrient release was observed during the anaerobic treatment step. Additionally, impurities removal causes a significant reduction of final nutrient content. Heavy metal analysis confirmed a high heterogeneity of contamination levels. However, digestion and composting do not seem to significantly impact on total heavy metal loads in the substrate flow.

6.2 Introduction

The biogas technology is one of the most promising approaches for the recovery of energy and fertilizer from municipal organic waste (MOW) (Appels et al., 2011). Within the last years, research and development as well as political incentives promoted MOW usage in biogas plants and the recycling of digestion residues (Saveyn and Eder, 2014). With over 8000 biogas plants installed (FNR, 2017). Germany ranks as a pioneer of biogas technology holding 31% of the worldwide capacity for biogas production in 2015 (IRENA, 2017). More than 100 biogas facilities have already specialized on MOW treatment (Kern et al., 2012) and further increase is expected due to resource scarcity and shift in subsidize policy (Schüch et al., 2016). Digestates are supposed to be redistributed to arable land to substitute synthetic fertilizers and to promote humus development (Insam et al., 2015; Nkoa, 2014; Odlare et al., 2015). However, there is still a gap of knowledge regarding digestate characteristics and complete mass and element balances from complex MOW treatment processes, which is addressed by this paper.

To estimate the ecological and the economic value of MOW digestates, to decide on post-treatment measures and to meet legal application requirements, digestate properties such as nutrient content, organic matter stability and contamination with heavy metals and impurities need to be known. The nutrient composition of digestates was investigated by several authors (Al Seadi et al., 2013; Risberg et al., 2017; Teglia et al., 2011b; Zirkler et al., 2014). Only few studies investigate properties of digestates from MOW treatment (Knoop et al., 2017; Odlare et al., 2015; Tampio et al., 2016). It can be summarized that digestates provide a broad range of nutrients, which however depends on the composition and treatment of feedstocks. MOW digestates may also contain heavy metals, impurities and organic pollutants (Govasmark et al., 2011; Kupper et al., 2014) and amendment products need to meet legal thresholds before they can be applied to agricultural land. Feedstock contamination with impurities mainly results from on-site miss-sorting and leads to spreading of heavy metals

and pollutants in the digestate. Electronic scrap, batteries, ink and paint as well as road sweepings, hoover bag content or plant pot soil can be sources for heavy metals in MOW (Smith, 2009). Consequently, the quality of digestates or amendments from MOW treatment is strongly predetermined by feedstock purity.

The fate of elements during anaerobic treatment was investigated by several authors (Banks et al., 2011; Bauer et al., 2009; Knoop et al., 2017; Massé et al., 2007; Möller and Müller, 2012; Pognani et al., 2012; Zirkler et al., 2014) showing that composition and availability of nutrients are changed during digestion due to mineralization and transformation processes. Others focused on the development of organic matter during anaerobic treatment (Abdullahi et al., 2008; Tambone et al., 2009) and stated that after digestion solid remains contain less accessible organic compounds of higher structural complexity. Additionally, digestate properties can be influenced by post-treatment (Bauer et al., 2009; Maynaud et al., 2017). Different mechanical, thermal and biological treatment options exist (Drosg et al., 2015). Solid-liquid separation divides nutrients bound to the solid matter from solubilized nutrients. Up to 70% of the nitrogen and potassium will be contained in the liquid fraction after separation with a screw extractor, whereas more than 50% of phosphorus remain in the solid residue (Bauer et al., 2009). Results also show that the choice of separator influences the nutrient content of digestates. Centrifuges have a higher removal efficiency for fine particles and therefore cause higher phosphorus contents in the solid phase (Møller, 2000). Drying of digestates leads to loss of volatile compounds especially ammonia (NH_3). Composting results in element enrichment due to further organic matter degradation and the formation of more stable and complex compounds and thereby changes the biochemical properties of digestates (Bustamante et al., 2013; Maynaud et al., 2017).

Summarizing the findings from literature, it becomes clear that feedstock composition as well as treatment before, during and after anaerobic digestion determine the properties of digestates. In turn, this facilitates to potentially

control final amendment characteristics and nutrient recovery by conscious management of feedstock composition and processing. In most cases, research on biogas technology focuses on improving the process with regard to biogas yields. So far, the quality of digestates was of minor interest. Recently, upcoming changes of legal restrictions for digestate spreading on agricultural land make digestate management inevitable for successful plant operation (Dahlin et al., 2015). Additionally, digestate properties become an important aspect with regard to marketing. However, only scarce information is available on how the treatment of feedstocks influences digestate properties and about what happens with initial nutrient and heavy metal loads during processing. So far, two studies have investigated mass and substance flows of organic waste during one-stage biogas processing and subsequent composting (Jensen et al., 2017; Pognani et al., 2012). There is still a gap of knowledge regarding complete element balances in complex biological treatment processes. Therefore, this study investigates properties of source-separated MOW before and after treatment in a semi-industrial scale biogas plant with two-stage digestion and subsequent composting of solid digestates. Data from 15 batch experiments using source-separated MOW was investigated by material and substance flow analysis (MFA/SFA) as described by Brunner and Rechberger (2004), and was analysed with the software STAN 2.5 by Cencic and Rechberger (2008). It is hypothesized that a share of nutrients and heavy metals contained in the feedstock is lost during treatment due to solubilization, deposition and volatilization of elements and material separation. Based on the results nutrient and heavy metal flows will be analysed and outputs of the entire process and each treatment step will be evaluated with regard to initial loads. Findings shall be used to optimize process performance and nutrient recovery for an efficient MOW management.

6.3 Materials and methods

6.3.1 Origin of MOW

For this study 15 different batches of separately collected municipal organic waste (MOW) were treated in a semi-industrial scale two-stage biogas plant followed by subsequent composting of solid digestates. Test series took place from 2013 to 2016. MOW originated from separate collection (biowaste bin) from a community in the vicinity of Dresden (Saxony, Germany) and was provided by a local composting facility. Prior to digestion, MOW was mixed with organic bulk material (10–15% of fresh matter) to ensure a high material porosity for percolation. Bulk material consisted of twigs and wood chips which are hardly degradable. It is removed at the end of the treatment and therefore a contribution to element flows during anaerobic and aerobic treatment is excluded. About 13 tons of fresh MOW feedstock were treated during each batch. Feedstock characteristics are described in Section 6.4.1 (Table 13).

6.3.2 Anaerobic treatment of MOW

MOW was treated in a semi-industrial scale two-stage biogas plant consisting of two anaerobic hydrolysis box fermenters (40 m^3), an anaerobic fixed-bed digester (14 m^3) and two percolate storage tanks. Each hydrolysis digester was filled with 6–7 tons of fresh feedstock and operated in batch under continuous percolation with process liquid. Percolate takes up dissolved compounds and was subsequently fed to the fixed-bed digester (carrier media: RVT-Bioflow 401) for methanation. Process temperature in the digesters was 37–40 °C. Retention time of MOW in the hydrolysis box fermenters was 14 days, which is shorter than in common biogas processes (> 21 days). A shorter retention time is intended by the plant operator due to a decrease of daily methane production towards the end of the process, which makes the extension of anaerobic treatment economically unfeasible. To monitor the biogas process, samples of process liquid were taken every day and analysed for pH (pH meter HQ40d Multi, Hach Lange), chemical oxygen demand (COD) (Merck cell test Spectroquant) and volatile organic acid

content (VOA) (acid titration). The amount and composition of biogas produced was measured daily by a gas meter (Ritter) and a gas analysis device (Visit 03, EHEIM). At the end of the digestion process percolation was stopped and digestate was drained. Liquid fraction was not treated and remained in the storage tanks of the biogas plant for percolation of following batches.

6.3.3 Post-treatment of MOW digestates

After 1–2 days of drainage, digestate was delivered to the composting plant, where it was treated in open heaps for 6–8 weeks. Substrate was turned over every 2 weeks. Process temperature in the heap was documented. Temperatures above 55 °C were reached during aerobic treatment ensuring hygienisation of substrates according to BioAbfV (§2). After composting, digestates were sieved in a drum screen at a mesh size of 20 mm to remove bulk material and impurities. The characteristics of solid digestate and composted digestate are described in Section 6.4.1.

6.3.4 Sampling and laboratory analysis of MOW and digestates

Samples of MOW, digestates and composted digestates have been investigated. To ensure representative sampling, up to 10 single samples of each piled batch were randomly taken and mixed to receive a composite sample, which was then homogenized and split to a sample size of 3–5 kg. Fresh samples were subsequently prepared for laboratory analysis. One third of the fresh sample was stored in the freezer. The rest was dried at 105 °C and impurities were removed. Afterwards, the sample was shredded in a laboratory cutting mill and subsequently ground in a mortar mill. The ground sample was homogenized by sieving at 0.25 mm.

Fresh samples were used to determine pH, plant available nitrogen (N_{pa} = NH_4-N+NO_3-N) and sample salinity according to the methods book of the German Federal Compost Association. pH and the content of N_{pa} were measured after 1 hour extraction of a 20 g sample (DM) with 200 ml $CaCl_2$ solution (0.01 mol l^{-1}) using a WTW pH meter (inoLab Multi 9620) and a Shimadzu

TN/TOC-Vcph-Analyzer. Sample salinity was determined after 1 hour extraction of a 20 g sample (DM) in 200 ml deionized water with a WTW meter (inoLab Multi 9620). All extractions were examined on a shaker at 100 rpm and extracts were filtered before measurement (Whatman cellulose filter N°1). Dry matter (DM) content of fresh samples was quantified after 24 hours drying at 105 °C in a laboratory oven (DIN EN 13040).

Methane potential (MP) was determined according to guideline 4630 of VDI (2006). Experimental setup of MP tests was done as described by Herrmann et al. (2011). Inoculum sludge was prepared as recommended by VDI (2006) and adapted to MOW feedstock during previous batch tests to ensure optimal test performance (Koch et al., 2017). Glass vessels were tempered at 37 °C in a heating oven. MP tests were performed in duplicate. Gas composition (CH_4, CO_2, O_2) was measured with a gas meter (ANSYCO, Biogas 5000). Data evaluation and MP calculation was done according to VDI (2006).

The residual MP of digestates (MP_r) in % was determined with the following formula:

$$MP_r = 100 - \frac{MP_{out} * VS_{out}}{MP_{in} * VS_{in}}$$

Equation 7: Residual methane potential of digestates (MP_r), MP_{in}; MP_{out} = Methane potential determined for feedstock (in) and digestate (out), VS_{in}; VS_{out} = Volatile solids content of feedstock (in) and digestate (out)

The dry and ground sample was used for the quantification of volatile solids (VS), total carbon (C), nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). The amount of VS was determined after 3 hours ignition of a 3 g sample (DM) at 550 °C in a muffle furnace (DIN EN 12879). C, N and S concentrations were measured after combustion of a 2 mg sample (DM) in an automatic CNS-Analyser (Vario EL III). Contents of P, K, Ca, Mg, Cd, Cr, Cu,

Ni, Zn and Pb were determined after pressure digestion of a 0.3 mg sample (DM) in aqua regia (DIN EN 13567) with ICP-OES (DIN EN ISO 11885).

All analyses were carried out in duplicate. All analysis results refer to the dry matter (DM).

6.3.5 Evaluation of analysis results

Analysis results of substrate samples from the 15 batches were checked for normal distribution by Kolmogorov-Smirnov test and for outliers by Dixon's Q test. Arithmetic mean and standard deviation for all samples of MOW, MOW feedstock, solid digestate, composted digestate and fine fraction of composted digestate were calculated and significant differences between means of data were tested by one-way ANOVA followed by Tukey test. Mean results from sample analysis (Table 13) were used for material flow analysis (MFA) and substance flow analysis (SFA) according to Brunner and Rechberger (2004). The visualization of the MFA model as well as substance flow calculation based on the inserted means and uncertainties was done with the software STAN 2.5 by Cencic and Rechberger (2008). The MFA model of MOW processing is shown in Figure 14. The spatial boundary of the system is defined by the MOW treatment chain, which is comprised of MOW pretreatment, anaerobic digestion, digestate composting and impurities and bulk material removal. There are two import flows MOW and organic bulk material, four export flows fine fraction of composted digestate, sieve overflow/bulk waste, biogas/process liquid, emissions/leachate and three internal flows MOW feedstock, solid digestate and composted digestate. To simplify the MFA model, there was no distinguishing between material and substances that leave the process as solubilized or volatilized compounds. The main focus was on the properties and flows of solid substrates during processing. All flows determined refer to a MOW input of 10 tons of fresh matter (FM).

Substance flows of the elements N, P, K, Mg, Ca, S, Cd, Cr, Cu, Ni, Pb and Zn were calculated with the formula:

$$SF = MF * DM * c$$

Equation 8: Substance flows (SF) in tons (for C), in kg (for nutrients) or in g (for heavy metals), MF = Mass flow in tons of FM, DM = Dry matter content of MF in % of FM, c = Substance concentration in % of DM

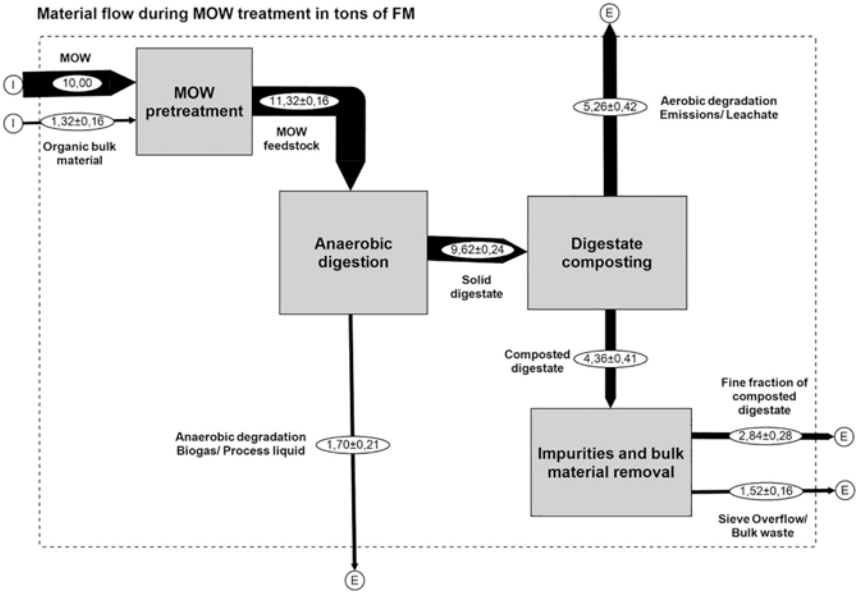

Figure 14: Overview of the investigated MOW treatment chain and relevant process flows in tons of fresh matter (FM)

Flow uncertainty is calculated in STAN 2.5 by taking into account the data uncertainty of each mean value inserted into the model. Data uncertainty (DU) of means was calculated as follows:

$$DU = \frac{SD}{\sqrt{n}}$$

Equation 9: Data uncertainty (DU), SD = Standard deviation of mean, n = Number of observations

Transfer coefficients (TC) are calculated to measure how much of a substance is transferred into a specific output. The following formula was applied:

$$TC = \frac{Output}{Input} * 100$$

Equation 10: Transfer coefficients (TC) in %, Output = Mass of substance × in tons, kg or g, Input = Mass of substance × in tons, kg or g

Based on the inserted data the export flows process liquid/biogas, emissions/leachate and sieve overflow/bulk waste were calculated by STAN 2.5. Of investigated elements only N, S and C can be volatilized (e.g. by forming NH_3, H_2S, CH_4, CO_2). Furthermore, it can be assumed that determined losses of nutrients and heavy metals occur due to solubilization and deposition (Möller and Müller, 2012), which will be further discussed in Sections 6.4.4 and 6.4.5.

6.4 Results and discussion

6.4.1 Results of substrate characterization throughout the treatment process

In Table 13, results from sample analysis and from literature review are presented. Analysis data for each sample type (MOW, MOW feedstock, solid digestate, composted digestate, fine fraction of composted digestate) is normally distributed. The evaluation of mean values shows that most of the investigated MOW properties undergo a significant change throughout the complete treatment process.

Obtained results for DM, VS, C and pH of MOW resemble the findings of Campuzano and González-Martínez (2016) who reviewed over 30 studies investigating MOW characteristics. During the investigated two-stage digestion volatile solids (VS) and carbon (C) content are lowered from 75.6%/39.0% to 68.0%/37.2%. In comparison, MOW-based digestates from other studies reveal lower VS and C contents (Jensen et al., 2017; Pognani et al., 2012; Stoknes et al., 2016; Tampio et al., 2016). This indicates that MOW degradation during the

investigated two-stage process is less intense. A significant reduction of VS and C was found during adjacent composting of solid digestates to 53.5%/28.6%. Furthermore, the DM content is significantly elevated during aerobic treatment (42.8%). Pognani et al. (2012), who also investigated organic waste degradation during anaerobic and subsequent aerobic treatment, determined a higher VS decrease during the digestion step. Reasons for a higher degradation during the anaerobic treatment step in Pognani et al. (2012) are a longer retention time (22 days) and thermophilic process conditions which are characterized by faster degradation rates. The pH of MOW was significantly elevated during the complete processing from 4.9 to 7.3 in the final product, which indicates the proceeded degradation of organic acids and maturation of the substrate. An average pH of 6.4 in the solid digestate matches the findings for VS and C contents, which altogether show that organic matter degradation is not completed after the investigated anaerobic treatment. However, this is intended by the plant operator to ensure a sufficient organic matter supply for adjacent composting and also with regard to the efficiency of the biogas process which will be further discussed in Section 6.4.2.

The results of sample characterization show that investigated MOW contains an average amount of 2.4% total N, 0.4% P, 1.1% K, 0.2% Mg, 2.5% Ca and 0.6% S in the DM. During treatment, nutrient contents are slightly elevated. However, differences between means are only significant for Mg ($\alpha = 0.05$). In contrary to our expectations, an explicit change in nutrient composition of samples cannot be confirmed during this study. This is also due to the high data variance within the sample types as expressed by high standard deviations (Table 13).

Table 13: Characteristics of samples from the complete MOW treatment chain in comparison to literature data (means of all samples +/- standard deviations, MOW= municipal organic waste; MOW feedstock = MOW mixed with organic bulk material; FM= fresh matter; DM= dry matter)

		Results from sample analysis					Results cited from literature		
		MOW	MOW + Bulk Material	Digestate	Composted Digestate	Composted + Sieved Digestate	MOW	MOW-based digestate	MOW-based compost
DM	% FM	31.2 +/- 2.1	33.7 +/- 2.5	29.4 +/- 2.8	42.8 +/- 3.9	43.6 +/- 6.1	27.2 +/- 7.6 [1]	29.9 +/- 2.1 [2,3,5,8]	49.7 +/- 16.4 [2,8,9]
VS	% DM	78.4 +/- 4.2	75.6 +/- 7.6	68.0 +/- 8.4	53.5 +/- 8.3	52.2 +/- 7.8	84.6 +/- 9.9 [1]	56.9 +/- 14.1 [2,3,8]	42.2 +/- 16.6 [2,8,9]
C	% DM	40.6 +/- 2.8	39.0 +/- 3.8	37.2 +/- 5.0	28.6 +/- 3.3	29.4 +/- 5.4	46.6 +/- 4.4 [1]	28.9 +/- 4.3 [3,8]	24.6 +/- 10.6 [7 (TOC)]
pH		4.9 +/- 0.3	-	6.4 +/- 0.7	-	7.3 +/- 0.3	5.2 +/- 0.95 [1]	7.8 +/- 0.7 [2,3]	7.7 +/- 0.8 [7]
Salinity	PSU	1.1 +/- 0.3	-	0.5 +/- 0.1	-	0.5 +/- 0.1	-	-	-
N		20.1 +/- 2.4	18.5 +/- 2.8	20.8 +/- 2.8	23.1 +/- 3.7	22.6 +/- 5.3	29.0 +/- 6.0 [1]	19.1 +/- 9.4 [2,3,8]	17.0 +/- 8.0 [7]
N_{an}		3.8 +/- 1.9	-	2.9 +/- 1.2	-	0.9 +/- 0.6	-	-	-
P		3.5 +/- 0.4	3.0 +/- 0.9	2.8 +/- 0.8	5.2 +/- 2.3	3.9 +/- 1.0	6.3 +/- 9.2 [1]	11.2 +/- 11.1 [2,8]	7.0 +/- 6.8 [7]
K	g kg^{-1} DM	10.6 +/- 0.6	10.1 +/- 1.7	9.7 +/- 2.1	10.9 +/- 1.3	11.1 +/- 0.9	9.1 +/- 4.0 [2,8]	9.9 +/- 1.6 [2,8]	9.0 +/- 8.5 [7]
Mg		2.1 +/- 0.7	2.6 +/- 0.9	3.0 +/- 1.3	4.9 +/- 0.8	4.9 +/- 0.9	1.5 +/- 0.1 [2,8]	4.1 +/- 2.3 [2,8]	3.3 +/- 0.7 [2,8]
Ca		24.8 +/- 4.5	21.0 +/- 2.7	26.8 +/- 6.6	34.0 +/- 10.3	34.0 +/- 9.8	18.5 +/- 7.7 [2,8]	44.3 +/- 25.8 [2,8]	35.4 +/- 9.1 [2,8]
S		5.5 +/- 0.7	5.5 +/- 2.0	5.7 +/- 1.6	6.2 +/- 1.1	6.9 +/- 1.8	3.0 +/- 2.6 [1]	2.0 [8]	1.3 [8]
Cd		1.4 +/- 0.9	1.0 +/- 0.6	1.4 +/- 0.8	3.0 +/- 1.9	2.0 +/- 1.0	0.2 +/- 0.12 [8]	0.4 +/- 0.4 [2,3,4,5,6,8]	0.5 +/- 0.2 [2,4,6,8]
Cr		15.0 +/- 6.8	15.6 +/- 4.8	26.6 -/+ 6.4	38.7 +/- 20.2	34.9 +/- 12.8	9.8 +/- 3.1 [2,8]	17.9 +/- 4.2 [2,3,4,5,6,8]	21.8 +/- 4.2 [2,4,6,8]
Cu	mg kg^{-1} DM	36.7 +/- 14.1	34.3 +/- 17.2	49.1 +/- 22.0	72.0 +/- 23.7	62.9 +/- 20.0	24.2 +/- 0.2 [2,8]	50.9 +/- 12.2 [2,3,4,5,6,8]	59.6 +/- 16.8 [2,4,6,8]
Ni		7.8 +/- 4.3	8.0 +/- 2.8	12.5 +/- 3.7	17.0 +/- 6.4	16.2 +/- 6.0	5.2 +/- 1.6 [2,8]	10.1 +/- 3.1 [2,3,4,5,6,8]	14.3 +/- 5.1 [2,4,6,8]
Pb		117.0 +/- 95.9	98.3 +/- 81.0	123.6 +/- 72.2	196.2 +/- 132.9	169.9 +/- 99.1	46.0 [8]	18.3 +/- 10.3 [2,4,5,6,8]	47.3 +/- 17.9 [4,6,8]
Zn		265.4 +/- 84.3	260.4 +/- 110.1	327.3 +/- 136.5	464.9 +/- 186.1	436.3 +/- 160.3	125.0 +/- 49.5 [2,8]	228.7 +/- 88.2 [2,3,4,5,6,8]	200.4 +/- 53.4 [2,4,6,8]
n		10	14	21	10	13			

1) Campuzano & González-Martínez (2016), 2) Stoknes et al. (2016), 3) Tampio et al. (2016), 4) Kupper et al. (2014), 5) Govasmark et al. (2011), 6) Saveyn & Eder (2014), 7) Faverial et al. (2016), 8) Jensen et al. (2017), 9) Pognani et al. (2012)

The fine fraction of composted digestates comprises an average amount of 2.4% total N, 0.4% P, 1.1% K, 0.5% Mg, 3.4% Ca and 0.7% S in the DM. The comparison of results on nutrient contents in the investigated substrates with literature data does not show significant differences (Table 13). However, the variability of data on properties of MOW-based digestates and composts from the literature review is high. Differences between nutrient contents of digestates and composts of this and other studies very likely result from variations in MOW composition due to regional and seasonal peculiarities (Campuzano and González-Martínez, 2016). This is also reflected by the results for MOW in Table 13. Furthermore, pretreatment and process conditions during treatment impact on nutrient characteristics in MOW-based products (Faverial et al., 2016).

Analysis of heavy metal contents of the investigated samples reveal an average amount of 1.4 mg kg^{-1} Cd, 15.0 mg kg^{-1} Cr, 36.7 mg kg^{-1} Cu, 7.8 mg kg^{-1} Ni, 117.0 mg kg^{-1} Pb and 265.4 mg kg^{-1} Zn in the DM of MOW. Thus, MOW contamination is clearly higher (except for Ni) than in other studies (Jensen et al., 2017; Stoknes et al., 2016). Sources for heavy metals in MOW can be impurities such as electronic scrap, batteries or paint but also soil and road sweepings (Smith, 2009). Pollution of MOW usually occurs at random (Kupper et al., 2014). However, results for Cd, Cr, Pb and Zn determined in substrates of this study seem to be generally higher than in other studies (Govasmark et al., 2011; Jensen et al., 2017; Kupper et al., 2014; Saveyn and Eder, 2014; Stoknes et al., 2016; Tampio et al., 2016). It is therefore assumed that higher heavy metal contents of investigated MOW batches are caused by regional peculiarities due to geological background exposure.

During anaerobic digestion and subsequent composting, heavy metal concentration rises in the investigated substrates. Finally, a significant accumulation in the fine fraction of composted digestate can be found for the elements Cr, Cu, Ni and Zn (α= 0.05). Heavy metals are non-biodegradable. Consequently, the degradation of organic matter leads to an accumulation of heavy metals in the solid residues. The fine fraction of composted digestates

contains an average amount of 2.0 mg kg^{-1} Cd, 34.9 mg kg^{-1} Cr, 62.9 mg kg^{-1} Cu, 16.2 mg kg^{-1} Ni, 169.9 mg kg^{-1} Pb and 436.3 mg kg^{-1} Zn in the DM. A higher heavy metal contamination of MOW subsequently results in process outputs with high heavy metal loads. This emphasizes that the quality of MOW-based amendments is strongly predetermined by feedstock purity, which to ensure shall be the first priority of MOW management.

6.4.2 Anaerobic treatment step and methane potential of feedstocks and digestates

Figure 15A summarizes the results from methane potential (MP) tests of investigated feedstocks. The average MP of MOW is 335 Nl kg^{-1} VS (SD = 34 Nl kg^{-1} VS). Obtained results range from 265 Nl kg^{-1} VS to 443 Nl kg^{-1} VS, confirming a high heterogeneity of the degradability of MOW samples. Campuzano and González-Martínez (2016) found an average methane yield of MOW of 415 Nl kg^{-1} VS (SD = 138 Nl kg^{-1} VS). However, the review also revealed a great variance of results depending on feedstock composition and experimental setup (Campuzano and González-Martínez, 2016). Pavi et al. (2017) determined an average methane yield of 180 Nl kg^{-1} VS during mesophilic batch tests with the organic fraction of municipal waste. Furthermore, Pavi et al. (2017) found that methane yields from MOW are higher (up to 400 Nl kg^{-1} VS) with an increased share of fruit and vegetable waste characterized by high contents of easily degradable carbohydrates. Koch et al. (2017) determined a MP of up to 460 Nl kg^{-1} VS for food waste. The variation in MOW composition with regard to the share of food waste influenced by seasonal changes, cooking habits and collection procedures is seen as the main reason for the high variation of methane yields from MOW.

The investigation of percolate parameters provides an insight into the progress of anaerobic treatment (Figure 16). On the second day of plant operation, the pH reaches its lowest level with 5.9 on average, which indicates a fast turnover of degradable substances into organic acids. However, pH values vary strongly during the first three days of plant operation depending on the content of easily

degradable matter in the feedstock and the buffering capacity of process liquid. The lowest pH result found during investigations was 4.4. Subsequent to the pH drop, values rise constantly until a level of 7.5 is reached on day eleven of plant operation indicating the decrease of acidification processes. The same is confirmed by the development of volatile organic acids (VOA) concentration in the percolate, which can be another indicator for the process development. During investigations on MOW digestion, a VOA peak was found between second and third day of plant operation reaching 4.3 g l^{-1} in the percolate at average. Due to VOA degradation in the fixed-bed digester, VOA content in the process liquid is lowered to a level of 1.3 g l^{-1} until day eleven of plant operation, which is about the same chronological sequence as for the pH. The chemical oxygen demand (COD) is the third percolate parameter investigated to evaluate the progress of anaerobic digestion. Highest peak was found in the percolate on day two with 15.2 g l^{-1} on average. Following, COD concentration was continuously lowered due to degradation processes. Correlation analysis (Table 14) shows that pH, VOA content and COD content of process liquid strongly correlate with each other (R > ±0.9).

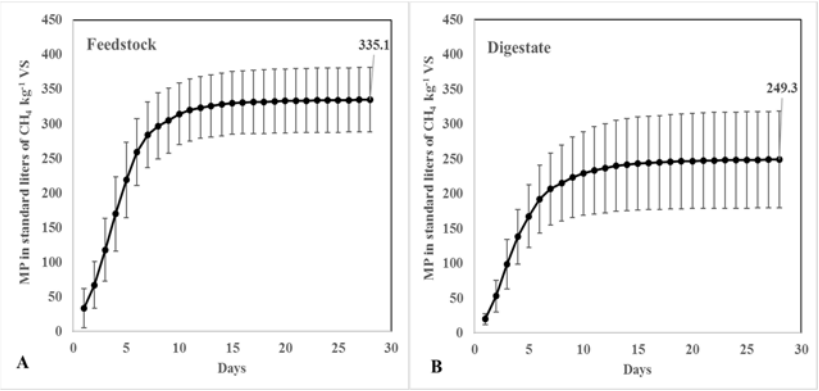

Figure 15: Cumulative methane potential of MOW feedstocks (A) and solid digestates (B) (MP= methane potential; VS= volatile solids)

To sum up results of percolate analysis, highest organic load and lowest pH was determined on days two and three of plant operation. Afterwards, degradation of organic compounds leads to a constant rise of pH and the decrease of VOA and COD concentration. Similar observations were reported by Pezzolla et al. (2017) who investigated percolate properties during solid state anaerobic digestion of a pig-slurry-straw-mixture. A rapid increase of VOA and/or VFA (volatile fatty acids) at the beginning is followed by a constant decrease (Massaccesi et al., 2013; Pezzolla et al., 2017). Rate and duration of percolate recirculation influence organic matter degradation (Pezzolla et al., 2017) and may be specifically regulated to increase process performance (Di Maria et al., 2016). Altogether, from day eleven of the investigated plant operation no significant change in percolate parameters can be observed indicating the finalisation of anaerobic treatment in the two-stage biogas plant. Therefore, the digestion was stopped after 14 days.

Table 14: Pearson correlation coefficients for percolate parameters pH, VOA (volatile organic acids), COD (chemical oxygen demand) and retention time (data is normally distributed, R = +/- 0.8-1.0 indicates a strong linear relationship)

Correlation [R]	Retention Time	pH	VOA	COD
Retention Time	1.00			
pH	0.66	1.00		
VOA	-0.66	-0.96	1.00	
COD	-0.72	-0.98	0.94	1.00

The average MP of investigated digestates from the two-stage biogas plant is 249 Nl kg^{-1} VS (SD = 69 Nl kg^{-1} VS) (see Figure 15B). Again, results from MP tests present a broad variation from 108 to 385 Nl kg^{-1} VS reflecting the heterogeneity of feedstocks. No MP results on MOW digestates were found. The MP results of investigated digestates are significantly higher than in other studies on conventional digestates (Sambusiti et al., 2015; Thygesen et al., 2014).

Thygesen et al. (2014) summarized that high MP of manure-based digestates (156–240 Nl kg^{-1} VS) were caused by short retention time (12–25 days).

Investigating the VS of feedstocks and digestates revealed an average VS degradation rate of 34% (SD = 8%). During two-stage anaerobic digestion of MOW at laboratory scale by Knoop et al. (2017), a maximum VS degradation of 62% was achieved within 32 days. Setting VS contents of feedstocks and digestates into relation to the results from MP tests, on average 53% (SD = 11%) of the MP of feedstocks have been depleted during investigated anaerobic treatment.

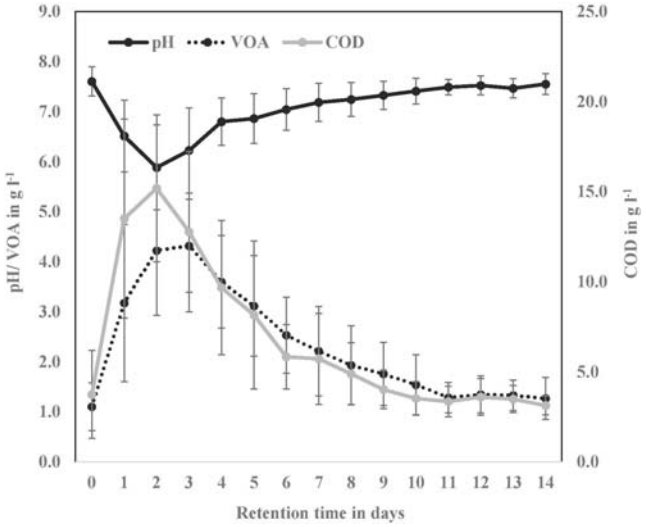

Figure 16: Development of percolate parameters pH, VOA and COD during anaerobic treatment of MOW

Results confirm that digestates of this study clearly have a degradation potential. However, during this investigation, relative methane yields were too low for an efficient plant operation after 14 days and remaining organic matter was successfully degraded during adjacent composting. Increasing the number of hydrolysis box fermenters and introducing a time-shifted digestion can be an option to compensate low daily biogas production of individual fermenters. This

would allow longer retention times and potentially lead to an increase of substrate degradation. In turn, this would lower the available organic matter for the aerobic biocoenosis during post-treatment and cause the need for an additional organic matter source for successful composting. Therefore, the evaluation and optimization of feedstock degradation during anaerobic treatment needs to be done with regard to the overall concept of complete MOW treatment.

6.4.3 Mass and carbon balance of complete MOW treatment

The mass balance of MOW treatment was standardized to an input of 10 tons of fresh MOW from separate collection (Figure 14). MOW is mixed with 1.3 tons of organic bulk material to reach an average 12% share in the feedstock, which shall optimize the flow of process liquid. Anaerobic digestion of pretreated MOW results in 9.6 tons of solid digestate, which is subsequently composted. After composting, 4.4 tons of composted digestate remain, which will be sieved to remove bulk material and impurities. Finally, process output is 2.8 tons of fine fraction of composted digestate. The highest mass loss was observed during composting due to the reduction of water content in the substrate (see Table 13). After treatment, 28% of 10 tons of MOW remain as final product available for further utilization. In comparison, Jensen et al. (2017) reported that 41% of total process input were left after complete treatment of source-separated organic household waste in a combined anaerobic and aerobic facility. Pognani et al. (2012) discovered 28% of the initial MOW input in the final compost, which resembles the findings of this study. Reasons for the differences in output mass can be either different moisture contents of flows, differences in separation efficiency during sieving or different degradation rates.

Carbon (C) flows indicate the extent of degradation during anaerobic and aerobic treatment (Figure 17). 10 tons of fresh MOW contain an average carbon content of 1.3 tons. After pretreatment, 1.5 tons of C enter the digestion process of which 1.0 tons of C remain in the solid digestate. 0.5 tons of C (33%) are degraded to CH_4 and/or CO_2 during anaerobic digestion. During composting

another 0.5 tons of C are converted into CO_2. 0.5 tons of C enter the last process step of impurities removal. 0.1 tons of C remain in the sieve overflow. Finally, 0.4 tons of C are contained in the fine fraction of composted digestate. Results show that the extent of C degradation is similar during anaerobic and subsequent aerobic treatment of this study.

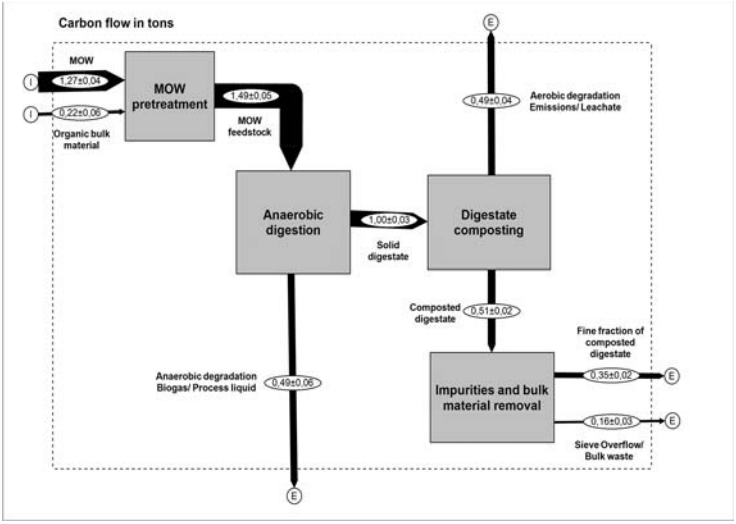

Figure 17: Carbon flow in tons during complete treatment of MOW

Altogether, 28% of the initial amount of C remain in the final product after complete MOW treatment (Table 15). Findings of this study are close to the findings of other studies investigating complete MOW processing. Jensen et al. (2017) discovered 23% of total C inflow in the final compost. Pognani et al. (2012) found 31% of initial C load in the final process outflow. However, the degradation of C during each step of biological treatment differs. C degradation during anaerobic treatment accounts for 24% in Jensen et al. (2017) and 39% during investigations of Pognani et al. (2012). On the contrary, C degradation during aerobic post-treatment was 40% of initial C load during investigations of Jensen et al. (2017) and up to 28% of initial C load in Pognani et al. (2012).

Altogether, the total C degradation is within the same range (64–67%) in all three studies.

Table 15: Transfer coefficients (TC) of investigates substances contained in MOW (TC relate output quantities to input quantities of investigated substances, see section 6.3.5)

TC	C	N	P	K	Mg	Ca	S	Cd	Cr	Cu	Ni	Pb	Zn
MOW feedstock vs. Solid digestate	67	79	66	68	81	90	73	96	120	101	111	89	89
Solid digestate vs. Composted digestate	51	73	123	74	108	84	72	137	96	97	90	105	94
MOW feedstock vs. Composted digestate	34	58	81	50	88	76	53	132	116	98	100	93	83
MOW vs. Fine fraction of composted digestate	28	43	42	40	89	52	48	53	89	65	79	55	63

6.4.4 Nutrient flows during MOW treatment

Figure 18 summarizes flows of nutrients N, P, K, Mg, Ca and S during complete MOW treatment. Table 15 shows transfer coefficients (TC) for all investigated elements. The main amount of nutrients was provided to the treatment system by MOW inflow. A small contribution was made by the organic bulk material. However, as the bulking agent consists of hardly degradable wood chips and twigs it is assumed that nutrient load introduced by it is removed through sieving at the end of the process chain.

On average, 10 tons of separately collected MOW contain 62.7 kg nitrogen (N). After pretreatment, 70.5 kg N enter anaerobic treatment of which on average 14.5 kg (21%) are mineralized during the digestion process. From a biochemical

point of view, N released during organic matter degradation can be expected to be either solubilized in the percolate or volatilized in the gaseous phase (Möller and Müller, 2012; Zirkler et al., 2014). Jensen et al. (2017) did not confirm N emissions in the biogas. This leads to the assumption that released N mainly accumulates as NH_4 in the percolate, where it remains solubilized or may bond with other free ions. A high NH_4 accumulation is underlined by findings of Akhiar et al. (2017), who determined N concentrations of up to 6.5 g l^{-1} in the liquid fraction of digestates. During composting another 14.8 kg N (27%) are released. Due to the pH increase in the substrate, mainly a volatilization of mineralized N in form of NH_3 is assumed. Additionally, 14.2 kg N remain in the sieve overflow after impurities removal.

The final process output contains 26.9 kg N (43% of initial N input). In comparison, N output of this study is lower than found by Jensen et al. (2017) who discovered 69% of initial N from process input in the compost after anaerobic and aerobic treatment of organic waste. Closer to the findings of this study are results by Pognani et al. (2012), who determined 50% of initial N load in compost resulting from anaerobic and aerobic treatment of organic waste. Both authors confirm high NH_3 emissions during the composting of digestates.

10 tons of MOW contain an average amount of 10.9 kg phosphorus (P). After mixing with bulk material, 11.4 kg P enter the digestion process of which 3.9 kg P (34%) are released during anaerobic treatment. Subsequent composting of solid digestates does not diminish P load of substrates as the calculation in STAN even resulted in a negative flow (−1.7 kg, TC = 123). It is impossible that total mass of P increases during aerobic treatment. The only possible explanation for the obtained result is the heterogeneity of MOW resulting in a non-homogeneous distribution of P in the composted digestate. Although the applied sampling methodology included several steps of sample homogenization and subsampling, data uncertainty is high (see Figure 18). Impurities removal leads to a loss of 4.6 kg P in the sieve overflow. Finally, the fine fraction of composted digestate contains 4.6 kg P (42% of initial P input).

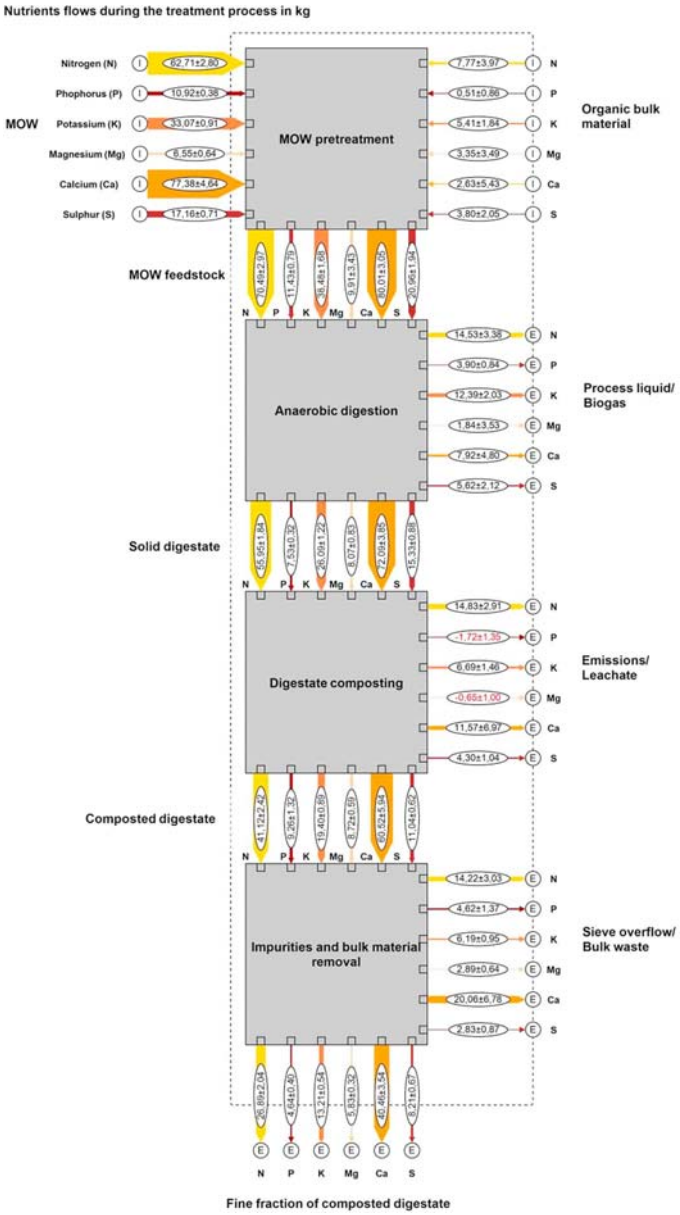

Figure 18: Nutrient flows in kg during complete treatment of MOW (investigated elements are highlighted by different arrow-colours)

In contrast to the findings of this study, Jensen et al. (2017) did not discover P losses during anaerobic treatment and determined the full initial P load in the composted digestate. The same result was found by Pognani et al. (2012), who detected the same amount of P_2O_5 in the feedstock and the final outflow. Consequently, P loss may be an effect occurring in two-stage systems due to the separation of solid and liquid phase during digestion and the discharge of elements with the percolate outflow. However, some studies which solely focus on anaerobic treatment of different feedstocks confirm losses of P due to its mineralization and subsequent deposition. In a study on the digestion of domestic food waste Banks et al. (2011) discovered a P reduction in the digestate of 67% of initial loads. A decrease of P was also reported by Massé et al. (2007) during pig manure digestion and by Knoop et al. (2017) during anaerobic treatment of MOW. P ions are very reactive. Losses of P may occur with losses of N and Mg which indicates struvite precipitation (Banks et al., 2011; Zirkler et al., 2014). Furthermore, P may precipitate as Ca-phosphate and Fe-phosphate (Möller and Müller, 2012). Thus, process conditions during anaerobic treatment of this study may have caused differences with regard to P distribution compared to Jensen et al. (2017) and Pognani et al. (2012). Regular percolation of feedstock is assumed to favour the outflow of nutrients especially at the beginning of the process, when the pH is low (see Figure 16). Consequently, P precipitates outside the hydrolysis box fermenters and cannot be recovered in the solid digestate.

On average, 33.1 kg potassium (K) are provided by 10 tons of MOW from separate collection. After pretreatment, 38.5 kg K enter the digestion process. From that 12.4 kg K (32%) are mineralized during the anaerobic treatment step. Another 6.7 kg K (26%) are released during composting. Sieving results in 6.2 kg K in the sieve overflow. Altogether, 40% of initial K load can be found in the final output flow of MOW processing. Findings from other studies show that mineralized K can mainly be found in the liquid phase of digestates (Akhiar et al., 2017; Bauer et al., 2009; Drosg et al., 2015). This results from the chemical properties of K, which is monovalent, highly reactive with water and does not form strong bonds or precipitates with other free anions. A share of K^+ may

adsorb to free exchange sites of negatively charged surfaces of residual organic matter in the digestate (Knoop et al., 2017). However, K adsorption is loose and K^+ are easily eluted again. K that cannot be rediscovered in the digestate is assumed to be retained in the percolate during digestion and in the leachate during composting.

Investigations on MOW samples show that on average 10 tons of MOW contain 6.6 kg magnesium (Mg). Anaerobic treatment leads to a release of 1.8 kg Mg (19%), which may contribute to struvite precipitation (Zirkler et al., 2014). However, struvite is formed if NH_4^+, PO_4^{3-} and Mg^{2+} are available in equal molar concentration. The release of Mg during the investigated anaerobic treatment is low and does not occur at the same extent as for N and P. Consequently, Mg is the limiting element for struvite precipitation. Therefore, this effect is assumed to be rather low and may occur only until all free Mg^{2+} are consumed. No Mg loss can be found during aerobic post-treatment (TC = 108). After impurities removal (−2.9 kg) the final output flow contains 5.8 kg Mg (89% of initial Mg load). All Mg flows are subject to relatively high data uncertainty (up to 3.5 kg, see Figure 18).

10 tons of MOW contain an average amount of 77.4 kg calcium (Ca). After pretreatment 80.0 kg Ca enter the digestion process step. 7.9 kg Ca (10%) are mineralized during anaerobic treatment and potentially contribute to precipitation of carbonate and Ca-phosphate (Chen et al., 2008). Subsequent composting of solid residue leads to the mineralization of 11.6 kg Ca (16%), which is assumed to be washed out with the leachate. Another 20.1 kg Ca remain in the bulk overflow after sieving. The final output flow comprises 40.5 kg Ca (52% of initial Ca load). However, Ca flows are subject to highest absolute data uncertainty (up to 7.0 kg). On average, 10 tons of MOW from separate collection contain 17.2 kg sulphur (S). After mixing with organic bulk material, 21.0 kg S enter the anaerobic digester. Then, 5.6 kg S (27%) are mineralized during anaerobic treatment. Organic matter degradation releases sulfate which may either volatilize as H_2S or precipitate as sulfide (Chen et al., 2008; Möller and

Müller, 2012). Furthermore, 4.3 kg S (28%) are lost during composting, which may to some extend also be caused by H_2S volatilization (Möller and Müller, 2012). Sieving leads to a removal of 2.8 kg S. Finally, the fine fraction of composted digestate contains 8.2 kg S (48% of initial S load).

Summarizing the findings from nutrient flow analysis of the complete treatment chain, it can be stated that the absolute nutrient release is higher (except for Ca) during two-stage anaerobic treatment than during subsequent aerobic treatment. It is assumed that this is caused by percolation, which forces a higher nutrient discharge into the process liquid. Additionally, acidic conditions during the first days of anaerobic treatment may enhance nutrient outflow as the availability of nutrient ions is higher at lower pH levels (Möller and Müller, 2012). Altogether, 23% of the nutrients (mainly N and K) contained in the MOW inflow are mineralized during anaerobic treatment. The degradation of organic matter during digestion leads to a biochemical conversion of organically bound nutrients. Released elements will subsequently be found in the process liquid, where they either remain solubilized or form new compounds of light and strong bonding depending on the element-specific binding affinity and available binding partners (Möller and Müller, 2012). It is assumed that in the two-stage biogas plant, a share of nutrients deposits outside the hydrolysis box digesters and therefore cannot be rediscovered in the solid digestate.

Another 18% of nutrient inflow from MOW are released during composting (mainly N) caused by volatilization or leachate runoff. Impurities removal by sieving leads to a loss of 35% of composted digestate inflow which remain as bulk waste in the sieve overflow and consequently cause an average nutrient loss of 35% at the end of the treatment process. Altogether, the fine fraction of composted digestate contains 48% of initial nutrient inflow from MOW. Nutrient outflow in the removed bulk waste after composting is double as high as the nutrient inflow from bulk material added during MOW pretreatment. Therefore, the treatment process shall be optimized with regard to sieving to minimize associated nutrient loss in the sieve overflow. A major factor will be

decreasing the moisture content of composted digestates to prevent clogging of fine particles and blocking of sieves. Higher DM contents of composted digestates may be reached by shielding of heaps to prevent seepage with rain water. This will additionally reduce leachate runoff during aerobic treatment.

6.4.5 Heavy metal balance

The investigation of heavy metal flows during MOW treatment shows that 10 tons of MOW from separate collection contain an average amount of 4.4 g cadmium (Cd), 46.9 g chromium (Cr), 114.4 g copper (Cu), 24.3 g nickel (Ni), 365.1 g lead (Pb) and 827.9 g zinc (Zn) (Figure 19). The addition of organic bulk material does not significantly change heavy metal loads entering the anaerobic treatment step. Transfer coefficients above 89% (Table 15) indicate that heavy metals largely remain in the solid phase during anaerobic and aerobic post-treatment. Organic matter degradation subsequently leads to an accumulation of heavy metals in the solid residues. Results on heavy metal contents show higher variances between means than results obtained during nutrient analysis. Only after sieving, a considerable reduction of total heavy metal loads can be observed caused by mass removal. The final process outflow contains from 53% (Cd) to 89% (Cr) of initial heavy metal load. The outflows process liquid/biogas and emissions/leachate are characterized by high data uncertainty and negative flow results. Furthermore, TC above 100 occur for Cd, Cr and Pb (see Table 15). An increase of the total mass of Cd, Cr and Pb is impossible during any biological treatment step. A TC above 100 results from high heterogeneity of heavy metal contents in the investigated batches (Table 13).

Summarizing the findings from heavy metal flow analysis, it can be concluded that digestion and composting do not seem to significantly impact on heavy metal loads in the substrate flow. However, obtained results are subject to very high data uncertainty limiting the validity of findings. During investigation on complete MOW treatment, Jensen et al. (2017) also found that all heavy metals passed through the facility and ended up in compost or residue. This leads to the assumption that the overall share of heavy metals in the inflow is present in stable

and non-soluble compounds. However, during a laboratory experiment on anaerobic digestion of MOW in a two-stage digester system with regular percolation and 30 days retention time by Knoop et al. (2017) highest potential heavy metal loss was detected for Cd, Pb and Zn, which are the same elements released during anaerobic treatment of this investigation. Acidic process conditions during anaerobic digestion favour heavy metal availability. Additionally, a release of heavy metals may be possible by dissolution of organic compounds during anaerobic digestion. Heavy metal ions form soluble organometallic complexes when binding to functional surface groups of dissolved organic carbon (DOC) (Christensen et al., 1996; Kunhikrishnan et al., 2017), which can be transported by percolation. High amounts of water-extractable carbon are released from fresh waste which is depending on the rate of mineralization of organic compounds (Said-Pullicino et al., 2007). Further research investigations are needed to evaluate heavy metal mobility during anaerobic treatment.

6.5 Conclusion

Results show that about 60% of nutrients contained in the MOW inflow can be retained in the process outflow during two-stage digestion and aerobic post-treatment. A higher nutrient release was observed during digestion forced by percolation and therefore recovery from the percolate may be an interesting option for plant operators. Results indicate that biological treatment does not seem to significantly impact on heavy metal loads in the substrate flow. However, due to high data heterogeneity the extent of heavy metal mobilization remains unclear. A low feedstock contamination needs to be striven to guarantee a high quality of MOW-based soil amendments.

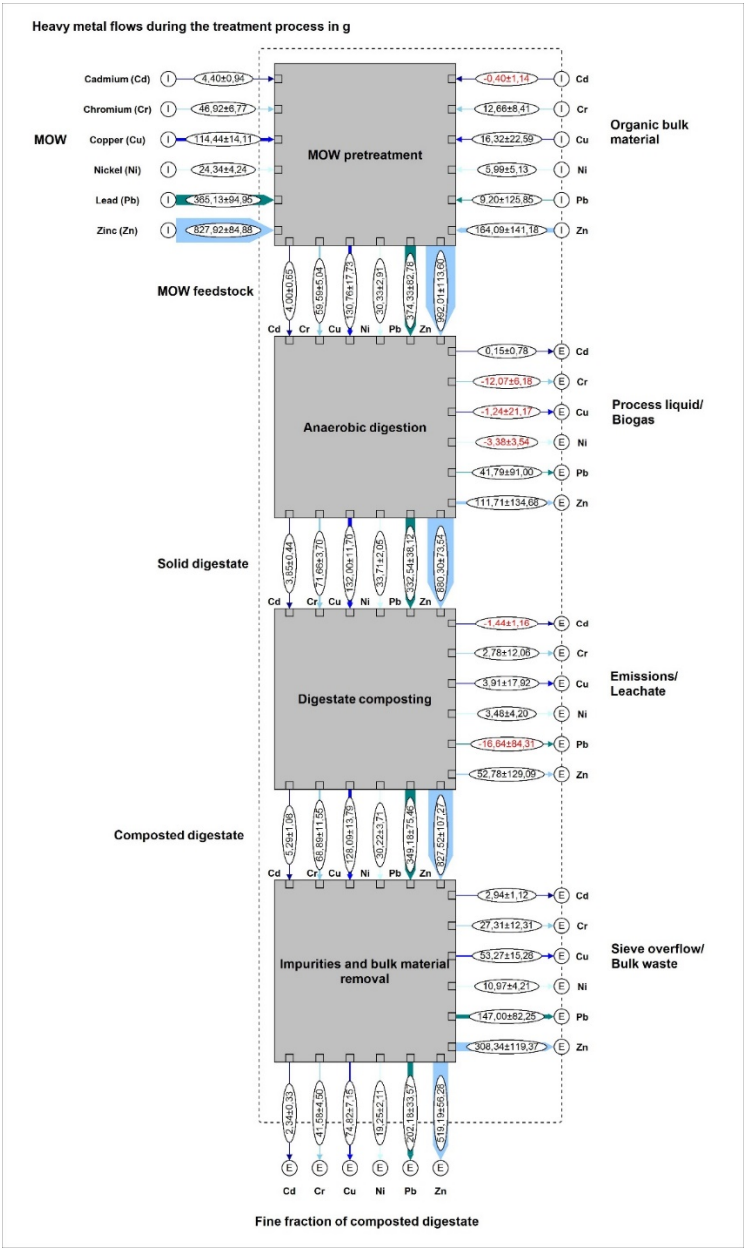

Figure 19: Heavy metal flows in g during complete treatment of MOW

7 Results synthesis and final conclusions

7.1 Synthesis of the results with regard to objectives and hypotheses

The provision of nutrients and organic matter to arable soils is critical to facilitate intensive agriculture and maintain soil functionality. However, nutrients which are sourced from mineral deposits such as P and K may become scarce in the future. Organic waste from municipalities is rich in nutrients and organic matter and presents a promising alternative to conventional fertilizers. Therefore, the recycling of these waste streams onto agricultural lands shall be given high priority over any other usage.

Before municipal organic waste (MOW) can be applied to soil certain quality criteria need to be fulfilled which are defined by international and national waste treatment and fertilizing legislations. The combination of anaerobic digestion and subsequent post-treatment has been identified as an ideal solution for the processing of MOW as it facilitates the recovery of both energy and a nutrient-rich organic soil amendment. While anaerobic digestion has been predominantly investigated with regard to biogas yields, the development of digestate properties during processing remained mainly unconsidered. Understanding how substrate composition changes during MOW treatment and identifying main substance flows during processing is important to evaluate and optimize recovery potentials. Therefore, the research objective of this thesis was to investigate the development of nutrient, heavy metal and organic matter content in MOW substrates during anaerobic digestion in a two-stage biogas plant and subsequent post-treatment. With this, knowledge gaps on digestate properties as well as on mass flows and nutrient recovery potentials during complete MOW treatment are intended to be filled.

7.1.1 MOW Quality

The first aspect of the thesis was the investigation of MOW properties, especially the evaluation of MOW quality with regard to treatment and recycling of process residues onto arable lands. Results show that MOW composition is rather heterogenic. This is indicated by a high variance of biogas yields and degradability as well as digestate properties. MOW composition also determines the availability and behavior of elements during biochemical conversion. The heterogeneity of nutrient composition (mean SD = 16%) is much lower than the heterogeneity of heavy metal contents (mean SD = 53%, see results section 6 Table 13). High heavy metal loads in MOW are related to high impurity contamination. A positive correlation ($R \geq 0.7$) was found between impurity contents and the concentration of Cd, Pb and Zn in the investigated MOW samples. Bilitewski and Härdtle (2013) confirm that especially plastics contribute to Cd, Pb and Zn contents in MOW. The impurity content of investigated MOW samples ranges from 0% to 12% proving the heterogenic results of heavy metal analysis. In comparison with other studies, heavy metal contents of MOW in this study seem to be generally higher. This leads to the assumption, that regional peculiarities such as geological background exposure could be another reason for high heavy metal contamination of MOW. Either way, results make clear that impurities and heavy metal contamination of MOW can become problematic when related products are supposed to be used as soil amendments. A few of the investigated MOW samples already exceed thresholds of BioAbfV for Cd, Pb and Zn. Therefore, besides nutrients the behavior of contaminants throughout the biological treatment process has been addressed by this thesis.

7.1.2 Influence of anaerobic treatment

Investigations on the influence of the anaerobic treatment in the two-stage biogas plant on digestate properties have been performed at laboratory and semi-industrial scale. Elements contained in MOW will either be mineralized during organic matter degradation or remain bound in the solid degradable-resistant matter. Mineralized elements are transported by percolate and will either remain

solubilized, bond to surfaces of existing molecular structures or form new compounds with other free ions. The distribution of elements during digestion depends on their availability, transport and binding affinity (Möller and Müller, 2012). Results from the laboratory experiments show that the nutrient and heavy metal concentration in the solid digestate is increasing during digestion except for N, P and Mg. The deficit of N, P and Mg amounts to the same extent (43-45%). If N, P and Mg are dissolved in equal molar ratio, a struvite precipitation can be expected (Le Corre et al., 2009). Furthermore, other phosphates, metal sulfides or carbonates may form together with other free ions, as there was also a deficit of Ca, Cd, Cr Ni, Pb and Zn in the solid digestate. During two-stage digestion, regular percolation transports mineralized elements from the location of release (hydrolysis digester) into storage tanks and the fixed-bed digester, where they may deposit. Low pH during acidification (pH = 4-6) favours element solubility and mobility. The pH milieu of the methanation stage (pH = 7-8) promotes precipitation processes. The transport of elements by percolation and the subsequent redistribution differentiates two-stage from one-stage systems. In contrast, K is the only investigated element which was completely rediscovered in the solid digestate during laboratory experiments. K is monovalent, does not form precipitates with other ions but easily bonds to free exchange sites of existing molecular structures. Therefore, mineralized K^+ are assumed to adsorb to solid matter and thereby enrich in the solid digestate during laboratory experiments.

Total element release was lower during semi-technical scale digestion, caused by shorter digestion of MOW, which consequently resulted in a lower VS degradation. A retention time of 14 days was intended by the plant operator due to small biogas yields at the end of the process. VS degradation during semi-technical scale digestion was 34% (Section 6). In comparison, during laboratory experiments a VS degradation of up to 62% was achieved in 32 days (Section 4). Results show that retention time influences element release and the nutrient content of the digestate. As an example, during semi-industrial scale anaerobic treatment the mineralization of Mg is lower and does not occur to the same

extent as for N and P. Consequently, Mg is the limiting element for struvite precipitation. Therefore, this effect may only occur until all free Mg^{2+} are consumed. Additionally, a shorter retention time significantly affects final K concentrations in the solid digestate. K enrichment in the solid digestate was not discovered during semi-technical scale experiments. In comparison, K contents were double as high in the digestate from the laboratory experiment. Therefore, it can be concluded that K enrichment depends on the degree of degradation achieved during anaerobic treatment. The complexity of the structure of the remaining organic matter in the digestate increases with the rate of degradation (Maynaud et al., 2017). Subsequently, a higher degradation rate leads to a greater number of exchange sites for K^{+}. Therefore, the effect of K adsorption is expected to occur only at longer retention times (> 25 days) under regular percolation with K-rich process liquid.

In comparison to nutrients, anaerobic treatment does not significantly impact total heavy metal loads in the substrate flow, which leads to the assumption that the overall share of heavy metals in MOW is present in stable compounds. However, results of laboratory investigations revealed a potential heavy metal release (<15%) for Cd, Cr, Pb and Zn. Acidic process conditions in the hydrolysis digesters can be assumed to favor heavy metal leaching. Heavy metal ions may bond to organic compounds by sorption and complexation. Especially dissolved organic carbon (DOC) can be a suitable binding partner for the development of soluble organometallic complexes. This facilitates the mobility of heavy metals in the percolate and may be a reason for the deficit in the solid digestate. Due to high data uncertainty the extent of heavy metal mineralization cannot be clearly estimated. However, as anaerobic treatment causes biochemical conversion of MOW, a shift of heavy metal availability can be expected, which bears the risk of increased heavy metal toxicity in the digestate. Even though impurities do not hamper the two-stage digestion process itself, their spreading during treatment can become problematic with regard to properties of soil amendments. To prevent this, impurities need to be removed in advance of any anaerobic treatment.

7.1.3 Influence of post-treatment

To estimate the influence of post-treatment, solid digestates from the semi-industrial scale biogas plant were processed by drying or composting as well as by subsequent sieving for impurities removal. Investigated digestates are characterized by a high residual degradation potential. The choice of post-treatment has a decisive impact on organic matter stability and the behavior of the amendment product.

Dried digestates are characterized by a lower concentration but higher elution of nutrients and heavy metals. Subsequently, soil amendments based on dried digestates would make a higher contribution to nutrient leaching and heavy metal availability in soil. In this context the elution of carbon, which was also higher from dried digestates, is important. DOC released from dried digestates will cause an increase of heavy metal bioavailability to plants. Therefore, organic matter stability is seen as a key factor for the performance of MOW-based amendments in soil. DOC elution is recommended to be used as a parameter for digestate quality evaluation. Composting leads to an improved organic matter stability. Composted digestates are characterized by higher nutrient and heavy metal concentrations, which result from further organic matter degradation and subsequent element accumulation. However, elution potential of composted digestates is much lower. Additionally, composted digestates have a higher cation exchange capacity, which reflects the increased structural complexity of organic matter.

From the viewpoint of soil, composted digestates shall be preferred as they deliver more nutrients and stable organic compounds. However, due to higher organic matter degradation, heavy metal accumulation can become a problem with regard to legislative thresholds. Sieving can even increase this problem as experiments with composted digestates revealed that heavy metals are not equally distributed. Highest heavy metal concentration was found in the fraction smaller than 1mm. Consequently, the removal of impurities and bulk material leads to further heavy metal accumulation in the digestate, as fractions with lower

contamination are refused in the sieve overflow. Experiments also show that sieving below 10 mm is needed to achieve the legal threshold of 0.5 % impurity content in the DM. However, this is related to a mass loss of up to 50%. Again, this emphasizes the importance of improved feedstock qualities, which will be further investigated in Section 7.2.1.

7.1.4 Evaluation of nutrient recovery potential from MOW

According to different potential studies the amount of MOW that may potentially be collected in on-site biowaste bins, is estimated to be up to 9 million tons year^{-1} (Fricke et al., 2013; Krause et al., 2014). Relating this number to the determined nutrient contents (section 6.4.1, Table 1), this results in 56.4 thousand tons of N, 9.8 thousand tons of P, 29.8 thousand tons of K, 5.9 thousand tons of Mg, 69.6 thousand tons of Ca and 15.4 thousand tons of S. N, P and K are the most important nutrients in agricultural production. According to statistics on annual nutrient demand in Germany in 2016/2017 (Industrieverband Agrar e.V., 2017), 9 million tons of on-site collected MOW could potentially cover 3.4% of annual demand for N, 9.7% of annual demand for P and 8.3% of annual demand for K. This is especially interesting with regard to P and K, which are mined from non-renewable sources and may become scarce in the future. To save fertilizer resources and to stay independent from price developments, recycling of nutrients from waste becomes an interesting option on regional levels.

Based on the substance flow analysis of section 6, 43% of N, 42% of P and 40% of K can be found in the soil amendment after investigated MOW processing. Subsequently, the produced soil amendment provides 1.5% of annual demand for N, 4.1% of annual demand for P and 3.3% of annual demand for K. Investigations on plant availability of nutrients (section 5.4.1) have shown that N availability is very low (2.6%) in composted digestates. Therefore, the produced soil amendment is not suitable for N-fertilization of crops and may only enhance long-term N-pools in soil. Plant availability of P in the composted digestate is up to 30%. Investigations on composts show that P will become available in soil by

100% (Kluge, 2008). The same can be assumed for K, of which up to 60% are already plant available in the short-term. Concluding, the final output of investigated MOW treatment is most suitable to complement P and K fertilization. Furthermore, Ca content of the produced soil amendment contributes to preservation liming. However, it may only cover 1.9% of annual agricultural demand for CaO (Industrieverband Agrar e.V., 2017).

7.2 Relevance and recommendations for practice

7.2.1 Improving MOW Quality

The first aspect reflected by the results of this thesis is the relevance of MOW quality, which will subsequently determine the quality and marketability of produced soil amendments. Impurities removal during MOW processing is limited and costly. Additionally, organic matter degradation during biological treatment leads to an accumulation of unwanted substances. Subsequently, treatment costs exceed benefits or MOW-based soil amendments cannot comply with legal requirements. Kehres (2016) from the German Federal Compost Association stated that the impurity content of MOW should be below 1 % of DM to enable an efficient production of high quality soil amendments. Investigated MOW samples have an impurity content of up to 12% in the DM, which clearly indicates potential for improvement.

Improving on-site collection is the best solution. Waste producers need to be sensitized and informed on how MOW can be recycled. The particular issue of impurities in MOW and the problems they cause during processing and further utilization of MOW-based products need to be communicated to them. Recently, different local campaigns have been initiated to encourage proper sorting and separate collection of MOW. Some of them are summarized in Figure 20. Various waste management companies, the German Federal Ministry of Environmental Protection, supermarkets, compost associations and non-governmental organizations are involved in these campaigns.

Figure 20: Recent campains to improve MOW purity

Another option to reduce impurities in MOW feedstock is the visual check-up of bins by disposal companies. Additionally, during initial trails, metal detectors installed on collection vehicles are used to identify contaminated bins (Maier & Fabris GmbH, 2017). Bins containing impurities will not be disposed and related households will be informed about collection requirements. Regional initiatives and campaigns to educate primary waste producers should be expanded throughout Germany. This shall also reduce lost MOW quantities in the residual waste bin (4.8 million tons year^{-1}, Kern and Siepenkothen, 2014) and thereby improve the recovery of MOW.

7.2.2 Improving nutrient recovery from MOW

There are three main possibilities for nutrient retention during processing: volatilization in the gaseous phase, dissolution in the liquid phase and precipitation. With regard to nutrient scarcity, the recovery of P may be most interesting for plant operators (Schaum, 2017). Experiments on laboratory scale (section 4) have shown that up to 45 % of P contained in the MOW feedstock are released during two-stage digestion. P anions ($P0_4^{3-}$) have a high binding affinity and are expected to form new compounds such as struvite

($(NH_4)Mg[PO_4]$) and other phosphates. Precipitated salts may be recovered from the sludge of storage containers and given back to enrich the solid digestate. This would be the simplest way to increase the recovery of N and P as well as other elements involved in precipitation. However, some aspects need to be considered. Firstly, Mg is usually the limiting factor for struvite precipitation and secondly, uncontrolled precipitation in the digester system may lead to process disturbances due to blocking of fermenter walls and pipes (Le Corre et al., 2009). The challenge is to integrate a controllable precipitation step into the existing anaerobic process. Crystallization is influenced by the pH, the supersaturation stage of the percolate, temperature and turbulence (Le Corre et al., 2009). These parameters need to be controlled to enable a precise struvite formation and must be matched with the process conditions of the two-stage anaerobic treatment. Proceedings for the removal of P are known from sewage sludge treatment (Montag et al., 2014; Müller, 2017; Schaum, 2017). AirPrex (Berliner Verfahren), Stuttgarter Verfahren, Gifhorner Verfahren and EloPhos are procedures for struvite recovery which have already been put into practice of waste water treatment plants in Germany (Müller, 2017). The sludge is enriched with magnesium chloride ($MgCl_2$) and the pH is elevated to over 8. After struvite has formed it can be removed from the process by e.g. a centrifuge. Afterwards, it needs to be washed to remove sludge particles by e.g. using a cyclone. Up to 95 % of dissolved P can be recovered by struvite precipitation (Montag et al., 2014). Integrating a P-recovery step in the storage tank after the methanation stage may be possible to remove P before the percolate is returned to hydrolysis. However, the increased pH of the percolate needs to be considered with regard to the lower pH optima of hydrolysis. Further research is needed to determine P concentrations in the percolate and the potential recovery rate as well as related process settings and costs.

Another option for the improvement of nutrient recovery during MOW processing is the capture of ammonia gas during digestate composting. This can be facilitated by filtering emissions in an acidic scrubber. During this process, ammoniac is captured in sulphuric acid solution. This leads to the formation of

highly concentrated ammonium sulfate solution, which can be used as liquid fertilizer. Commonly, chemical scrubbers are applied to remove pollutants and odors from gas streams in livestock farming. Their utilization will subsequently increase N recovery and prevents the release of unwanted nitrogen gases that contribute to acid rain formation. Results have shown that on average 24% of N contained in the MOW inflow is released during composting. This emphasizes the relevance of N capture during anaerobic treatment. Further research is needed to investigate recovery rates under practical conditions.

Finally, improving the sieving step with regard to a higher mass output will subsequently lead to a higher nutrient recovery from the treatment process. Sieving efficiency depends on the moisture content of composted digestates (Raussen and Kern, 2016). A high moisture content of the substrate causes clogging of fine particles, which will subsequently lead to higher sieve overflow. Raussen and Kern (2016) recommend a moisture content of 40% to ensure an efficient separation. In comparison, the moisture content of composted digestates investigated is 57% on average. This may be improved by prolonging the composting process, by roofing of heaps to prevent wetting of substrate from rainfall during treatment or by enhancing the aerobic process conditions by the additional supply of air and heat. The moisture content of composted digestates shall be evaluated before sieving to ensure an efficient substrate recovery.

7.3 Future research

Although different attempts can be made to improve MOW quality, 100% substrate purity is unlikely and pollutants in the process outflow will remain an issue. However, knowing their concentration is only one of many aspects. Further research is needed to understand how contaminants such as heavy metals but also organic pollutants are converted and mobilized during biological treatment and to evaluate the ecotoxicological potential of these substances when applied to soil.

Furthermore, the recovery of nutrients which are mineralized during anaerobic treatment shall be investigated. Results show that two-stage digestion with regular percolation favours the outflow of nutrients. Recycling nutrients dissolved in the percolate may be a worthwhile issue. Future research may aim on controlling element precipitation and the procedural integration of nutrient recovery into the two-stage system.

References

Abdullahi, Y.A., Akunna, J.C., White, N.A., Hallett, P.D., Wheatley, R., 2008. Investigating the effects of anaerobic and aerobic post-treatment on quality and stability of organic fraction of municipal solid waste as soil amendment. Bioresource Technology 99, 8631–8636. 10.1016/j.biortech.2008.04.027.

Abubaker, J., Cederlund, H., Arthurson, V., Pell, M., 2013. Bacterial community structure and microbial activity in different soils amended with biogas residues and cattle slurry. Applied Soil Ecology 72, 171–180. 10.1016/j.apsoil.2013.07.002.

Akhiar, A., Battimelli, A., Torrijos, M., Carrere, H., 2017. Comprehensive characterization of the liquid fraction of digestates from full-scale anaerobic co-digestion. Waste management (New York, N.Y.) 59, 118–128. 10.1016/j.wasman.2016.11.005.

Al Seadi, T., Drosg, B., Fuchs, W., Rutz, D., Janssen, R., 2013. 12 - Biogas digestate quality and utilization A2 - Wellinger, Arthur, in: Wellinger, A., Baxter, D., Murphy, J. (Eds.), The biogas handbook. Science, production and applications. Woodhead Publishing Limited, Oxford, pp. 267–301.

Al-Bataina, B.B., Young, T.M., Ranieri, E., 2016. Effects of compost age on the release of nutrients. International Soil and Water Conservation Research 4, 230–236. 10.1016/j.iswcr.2016.07.003.

Alburquerque, J.A., La Fuente, C. de, Campoy, M., Carrasco, L., Nájera, I., Baixauli, C., Caravaca, F., Roldán, A., Cegarra, J., Bernal, M.P., 2012a. Agricultural use of digestate for horticultural crop production and improvement of soil properties. European Journal of Agronomy 43, 119–128. 10.1016/j.eja.2012.06.001.

Alburquerque, J.A., La Fuente, C. de, Ferrer-Costa, A., Carrasco, L., Cegarra, J., Abad, M., Bernal, M.P., 2012b. Assessment of the fertiliser potential of digestates from farm and agroindustrial residues. Biomass and Bioenergy 40, 181–189. 10.1016/j.biombioe.2012.02.018.

Ali, G., Nitivattananon, V., Abbas, S., Sabir, M., 2012a. Green waste to biogas: Renewable energy possibilities for Thailand's green markets. Renewable and Sustainable Energy Reviews 16, 5423–5429. 10.1016/j.rser.2012.05.021.

Ali, I., Asim, M., Khan, T.A., 2012b. Low cost adsorbents for the removal of organic pollutants from wastewater. Journal of environmental management 113, 170–183. 10.1016/j.jenvman.2012.08.028.

Amlinger, F., Pollak, M., Favino, E., 2004. Heavy metals and organic compounds from wastes used as organic fertilizers. Final Report.

Antoniadis, V., Alloway, B.J., 2002. The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. Environmental Pollution 117, 515–521. 10.1016/S0269-7491(01)00172-5.

Appels, L., Lauwers, J., Degrève, J., Helsen, L., Lievens, B., Willems, K., van Impe, J., Dewil, R., 2011. Anaerobic digestion in global bio-energy production: Potential and research challenges. Renewable and Sustainable Energy Reviews 15, 4295–4301. 10.1016/j.rser.2011.07.121.

AGEE-Stat (Arbeitsgruppe Erneuerbare Energien-Statistik), 2016. Entwicklung der erneuerbaren Energien in Deutschland im Jahr 2015: Grafiken und Diagramme unter Verwendung aktueller Daten der Arbeitsgruppe Erneuerbare Energien-Statistik (AGEE-Stat). http://www.bmwi.de/DE/Themen/Energie/Erneuerbare-Energien/erneuerbare-energien-auf-einen-blick,did=645890.html. Accessed 8 December 2016.

Awiszus, S., Meissner, K., Reyer, S., Müller, J., 2018. Ammonia and methane emissions during drying of dewatered biogas digestate in a two-belt

conveyor dryer. Bioresource Technology 247, 419–425. 10.1016/j.biortech.2017.09.099.

Banks, C.J., Chesshire, M., Heaven, S., Arnold, R., 2011. Anaerobic digestion of source-segregated domestic food waste: Performance assessment by mass and energy balance. Bioresource Technology 102, 612–620. 10.1016/j.biortech.2010.08.005.

Bauer, A., Mayr, H., Hopfner-Sixt, K., Amon, T., 2009. Detailed monitoring of two biogas plants and mechanical solid-liquid separation of fermentation residues. Journal of biotechnology 142, 56–63. 10.1016/j.jbiotec.2009.01.016.

Bauermeister, U., 2015. Möglichkeiten für Nährstoffrückgewinnung und Wertschöpfungsketten mit dem Verfahren zur Faulschlamm -und Gärrestaufbereitung System GNS. http://www.metastream-netzwerk.de/fileadmin/contents/images/News/3_Bauermeister-Pr%C3%A4sentation_zum_29.04.2015.pdf. Accessed 28 January 2018.

BGK (Bundesgütegemeinschaft Kompost e.V.) (Ed.), 2006. Methodenbuch zur Analyse organischer Düngemittel, Bodenverbesserungsmittel und Substrate, 5th ed. Bundesgütegemeinschaft Kompost, Köln.

BGK (Bundesgütegemeinschaft Kompost e.V.), 2016. Auswertung der gütegesicherten Kompostanalysen 2015. http://www.kompost.de/fileadmin/user_upload/Dateien/Kompost_D_2015.pdf. Accessed 2 February 2017.

Bilitewski, B., Härdtle, G., 2013. Abfallwirtschaft: Handbuch für Praxis und Lehre, 4th ed. Springer Vieweg, Berlin, Heidelberg.

Blume, H.-P., Brümmer, G.W., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., Wilke, B.-M., 2016. Scheffer/Schachtschabel Soil Science, 1st ed. Springer Berlin Heidelberg, Berlin, Heidelberg, 123-174.

Bolzonella, D., Fatone, F., Gottardo, M., Frison, N., 2017. Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full-scale applications. Journal of environmental management. 10.1016/j.jenvman.2017.08.026.

Booker, N.A., Priestley, A.J., Fraser, I.H., 2010. Struvite Formation in Wastewater Treatment Plants: Opportunities for Nutrient Recovery. Environmental Technology 20, 777–782. 10.1080/09593332008616874.

Braguglia, C.M., Gallipoli, A., Gianico, A., Pagliaccia, P., 2017. Anaerobic bioconversion of food waste into energy: A critical review. Bioresource Technology. 10.1016/j.biortech.2017.06.145.

Brunner, P.H., Rechberger, H., 2004. Practical handbook of material flow analysis. Lewis Publ, Boca Raton Fla. u.a., 35-159.

Bustamante, M.A., Restrepo, A.P., Alburquerque, J.A., Pérez-Murcia, M.D., Paredes, C., Moral, R., Bernal, M.P., 2013. Recycling of anaerobic digestates by composting: Effect of the bulking agent used. Journal of Cleaner Production 47, 61–69. 10.1016/j.jclepro.2012.07.018.

Callander, I.J., Barford, J.P., 1983. Precipitation, chelation, and the availability of metals as nutrients in anaerobic digestion. I. Methodology. Biotechnology and bioengineering 25, 1947–1957. 10.1002/bit.260250805.

Cambier, P., Pot, V., Mercier, V., Michaud, A., Benoit, P., Revallier, A., Houot, S., 2014. Impact of long-term organic residue recycling in agriculture on soil solution composition and trace metal leaching in soils. The Science of the total environment 499, 560–573. 10.1016/j.scitotenv.2014.06.105.

Campuzano, R., González-Martínez, S., 2016. Characteristics of the organic fraction of municipal solid waste and methane production: A review. Waste Management 54, 3–12. 10.1016/j.wasman.2016.05.016.

Cencic, O., Rechberger, H., 2008. Material Flow Analysis with Software STAN. Journal of Environmental Engineering and Management 18, 291–298.

Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: A review. Bioresource Technology 99, 4044–4064. 10.1016/j.biortech.2007.01.057.

Christensen, J.B., Christensen, T.H., 2000. The effect of pH on the complexation of Cd, Ni and Zn by dissolved organic carbon from leachate-polluted groundwater. Water Research 34, 3743–3754. 10.1016/S0043-1354(00)00127-5.

Christensen, J.B., Jensen, D.L., Christensen, T.H., 1996. Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. Water Research 30, 3037–3049. 10.1016/S0043-1354(96)00091-7.

Dahlin, J., Herbes, C., Nelles, M., 2015. Biogas digestate marketing: Qualitative insights into the supply side. Resources, Conservation and Recycling 104, 152–161. 10.1016/j.resconrec.2015.08.013.

Davidsson, Å., Gruvberger, C., Christensen, T.H., Hansen, T.L., La Jansen, J.C., 2007. Methane yield in source-sorted organic fraction of municipal solid waste. Waste Management 27, 406–414. 10.1016/j.wasman.2006.02.013.

Delzeit, R., Kellner, U., 2013. The impact of plant size and location on profitability of biogas plants in Germany under consideration of processing digestates. Biomass and Bioenergy 52, 43–53. 10.1016/j.biombioe.2013.02.029.

Destatis, 2017. GENESIS-Online Datenbank: Bioabfall. https://www-genesis.destatis.de/genesis/online;jsessionid=420F41B128A95673BE7FA150BD12CCCB.tomcat_GO_1_2?operation=previous&levelindex=2&levelid=1504885827390&step=2. Accessed 10 December 2017.

Di Maria, F., Segoloni, E., Pezzolla, D., 2016. Solid anaerobic digestion batch of bio-waste as pre-treatment for improving amendment quality: The effect of

inoculum recirculation. Waste management (New York, N.Y.) 56, 106–112. 10.1016/j.wasman.2016.05.024.

Drosg, B., Fuchs, W., Al Seadi, T., Madsen, M., Linke, B., 2015. Nutrient Recovery by Biogas Digestate Processing. IEA Bioenergy.

Ellison, S.L.R., Farrant, T.J.D., Barwick, V.J., 2009. Practical statistics for the analytical scientist: A bench guide, 2nd ed. RSC Publishing, Cambridge, XIV, 1-268.

Facchin, V., Cavinato, C., Fatone, F., Pavan, P., Cecchi, F., Bolzonella, D., 2013. Effect of trace element supplementation on the mesophilic anaerobic digestion of foodwaste in batch trials: The influence of inoculum origin. Biochemical Engineering Journal 70, 71–77. 10.1016/j.bej.2012.10.004.

FNR (Fachagentur für Nachwachsende Rohstoffe), 2017. Bioenergy in Germany - Facts and Figures 2016. http://www.fnr.de/fileadmin/allgemein/pdf/broschueren/Broschuere_Basisdaten_Bioenergie_englisch_2017.pdf. Accessed 31 July 2017.

Fang, W., Delapp, R.C., Kosson, D.S., van der Sloot, Hans A., Liu, J., 2017. Release of heavy metals during long-term land application of sewage sludge compost: Percolation leaching tests with repeated additions of compost. Chemosphere 169, 271–280. 10.1016/j.chemosphere.2016.11.086.

Faverial, J., Boval, M., Sierra, J., Sauvant, D., 2016. End-product quality of composts produced under tropical and temperate climates using different raw materials: A meta-analysis. Journal of environmental management 183, 909–916. 10.1016/j.jenvman.2016.09.057.

Fraunhofer- IGB, 2016. Presseinformation - Gülle liefert Mineraldünger und Bodenverbesserer. https://www.igb.fraunhofer.de/content/dam/igb/de/documents/pressemitteilungen/2016/PI_1604_bioecosim_de.pdf. Accessed 28 January 2018.

Fricke, K., Heußner, C., Hüttner, A., Turk, T., Bauer, W., Bidlingmaier, W., 2013. Vergärung von Biound Grünabfällen - Teil 1: Ausbaupotenzial bei der Vergärung von Bio- und Grünabfällen. Müll und Abfall 45 (12), 625–680.

Fricke, K., Heußner, C., Hüttner, A., Turk, T., Barnemann, D., Pereira, C., Bauer, W., Bidlingmaier, W., 2014a. Vergärung von Bio- und Grünabfällen, Teil 3: Maßnahmen zur Verbesserung der Funktionalität und Energieeffizienz bei der Vergärung von Bio- und Grünabfällen. Müll und Abfall, 116–125.

Fricke, K., Heußner, C., Hüttner, A., Turk, T., Pereira, C., Bauer, W., Bidlingmaier, W., 2014b. Vergärung von Bio- und Grünabfällen, Teil 2: Status quo der Bio- und Grünabfallvergärung. Müll und Abfall 46, 1–52.

Fuchs, W., Drosg, B., 2013. Assessment of the state of the art of technologies for the processing of digestate residue from anaerobic digesters. Water Science and Technology 67, 1984–1993. 10.2166/wst.2013.075.

Fuentes, A., Lloréns, M., Sáez, J., Aguilar, M.I., Pérez-Marín, A.B., Ortuño, J.F., Meseguer, V.F., 2006. Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilised sewage sludges. Environmental Pollution 143, 355–360. 10.1016/j.envpol.2005.11.035.

Govasmark, E., Stäb, J., Holen, B., Hoornstra, D., Nesbakk, T., Salkinoja-Salonen, M., 2011. Chemical and microbiological hazards associated with recycling of anaerobic digested residue intended for agricultural use. Waste Management 31, 2577–2583. 10.1016/j.wasman.2011.07.025.

Hansen, T.L., La Cour Jansen, J., Spliid, H., Davidsson, Å., Christensen, T.H., 2007. Composition of source-sorted municipal organic waste collected in Danish cities. Waste Management 27, 510–518. 10.1016/j.wasman.2006.03.008.

Herrmann, C., Heiermann, M., Idler, C., 2011. Effects of ensiling, silage additives and storage period on methane formation of biogas crops. Bioresource Technology 102, 5153–5161. 10.1016/j.biortech.2011.01.012.

Huerta-Pujol, O., Soliva, M., Giró, F., López, M., 2010. Heavy metal content in rubbish bags used for separate collection of biowaste. Waste Management 30, 1450–1456. 10.1016/j.wasman.2010.03.023.

Insam, H., Gómez-Brandón, M., Ascher, J., 2015. Manure-based biogas fermentation residues – Friend or foe of soil fertility? Soil Biology and Biochemistry 84, 1–14. 10.1016/j.soilbio.2015.02.006.

IRENA, 2017. Renewable Energy Statistics 2017, Abu Dhabi. http://www.irena.org/DocumentDownloads/Publications/IRENA_RE_Capacity_Statistics_2017.pdf. Accessed 31 July 2017.

Jensen, M.B., Møller, J., Scheutz, C., 2017. Assessment of a combined dry anaerobic digestion and post-composting treatment facility for source-separated organic household waste, using material and substance flow analysis and life cycle inventory. Waste management (New York, N.Y.) 66, 23–35. 10.1016/j.wasman.2017.03.029.

Kehres, B., 2016. BGK-Standpunkt: Sortenreinheit von Bioabfällen gewährleisten.

Kern, M., Raussen, T., 2014. Biogas-Atlas, 1st ed. Witzenhausen-Institut für Abfall, Umwelt und Energie GmbH, Witzenhausen, 19-28.

Kern, M., Raussen, T., Graven, T., Bergs, C.-G., Hermann, T., 2012. Ecologically sustainable recovery of bio-waste: Suggestions for policy-makers at local authorities.

Kern, M., Siepenkothen, J., 2014. Bioabfallpotential im Hausmülle - Modellbetrachtung zur Steigerung der Erfassung von Bioabfällen aus dem Hausmüll. Müll und Abfall 46, 356–360.

Khalid, A., Arshad, M., Anjum, M., Mahmood, T., Dawson, L., 2011. The anaerobic digestion of solid organic waste. Waste management (New York, N.Y.) 31, 1737–1744. 10.1016/j.wasman.2011.03.021.

Khokhotva, O., Waara, S., 2010. The influence of dissolved organic carbon on sorption of heavy metals on urea-treated pine bark. Journal of Hazardous Materials 173, 689–696. 10.1016/j.jhazmat.2009.08.149.

Kim, M., Ahn, Y.-H., Speece, R.E., 2002. Comparative process stability and efficiency of anaerobic digestion; mesophilic vs. thermophilic. Water Research 36, 4369–4385. 10.1016/S0043-1354(02)00147-1.

Kluge, R., 2008. Projektbericht: Inhaltsstoffe von Gärprodukten und Möglichkeiten zu ihrer geordneten pflanzenbaulichen Verwertung.

Knoop, C., Dornack, C., Raab, T., 2017. Nutrient and heavy metal accumulation in municipal organic waste from separate collection during anaerobic digestion in a two-stage laboratory biogas plant. Bioresource Technology 239, 437–446. 10.1016/j.biortech.2017.05.026.

Koch, K., Lippert, T., Drewes, J.E., 2017. The role of inoculum's origin on the methane yield of different substrates in biochemical methane potential (BMP) tests. Bioresource Technology 243, 457–463. 10.1016/j.biortech.2017.06.142.

Krause, P., Oetjen-Dehne, R., Dehne, I., Dehnen, D., Erchinger, H., 2014. Verpflichtende Umsetzung der Getrenntsammlung von Bioabfällen: Forschungsbericht. 84/2014.

Kunhikrishnan, A., Choppala, G., Seshadri, B., Wijesekara, H., Bolan, N.S., Mbene, K., Kim, W.-I., 2017. Impact of wastewater derived dissolved organic carbon on reduction, mobility, and bioavailability of As(V) and Cr(VI) in contaminated soils. Biogeochemistry of trace elements in the environment 186, Part 2, 183–191. 10.1016/j.jenvman.2016.08.020.

Kupper, T., Bürge, D., Bachmann, H.J., Güsewell, S., Mayer, J., 2014. Heavy metals in source-separated compost and digestates. Waste Management 34, 867–874. 10.1016/j.wasman.2014.02.007.

Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Parsons, S.A., 2009. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. Critical Reviews in Environmental Science and Technology 39, 433–477. 10.1080/10643380701640573.

Leinweber, P., Reuter, G., Brozio, K., 1993. Cation exchange capacities of organo-mineral particle-size fractions in soils from long-term experiments. Journal of Soil Science 44, 111–119. 10.1111/j.1365-2389.1993.tb00438.x.

Lewis, A.E., 2010. Review of metal sulphide precipitation. Hydrometallurgy 104, 222–234. 10.1016/j.hydromet.2010.06.010.

Lorenz, F., Baumgärtel, G., Luyten-Naujoks, K., Olfs, H.-W., Schäfer, B., Roßberg, R., Erdle, K., 2014. DLG-Merkblatt 397 - Gärreste im Ackerbau effizient nutzen.

Maier & Fabris GmbH, 2017. Leitfaden zur Einführung des elektronischen Detektionssystems: Praktisch Tipps für Einsatzleiter und Abfallberater.

Massaccesi, L., Sordi, A., Micale, C., Cucina, M., Zadra, C., Di Maria, F., Gigliotti, G., 2013. Chemical characterisation of percolate and digestate during the hybrid solid anaerobic digestion batch process. Process Biochemistry 48, 1361–1367. 10.1016/j.procbio.2013.06.026.

Massé, D.I., Croteau, F., Masse, L., 2007. The fate of crop nutrients during digestion of swine manure in psychrophilic anaerobic sequencing batch reactors. Bioresource Technology 98, 2819–2823. 10.1016/j.biortech.2006.07.040.

Maurer, C., Müller, J., 2012. Ammonia (NH3) emissions during drying of untreated and dewatered biogas digestate in a hybrid waste-heat/solar dryer. Engineering in Life Sciences 12, 321–326. 10.1002/elsc.201100113.

Maynaud, G., Druilhe, C., Daumoin, M., Jimenez, J., Patureau, D., Torrijos, M., Pourcher, A.-M., Wéry, N., 2017. Characterisation of the biodegradability of post-treated digestates via the chemical accessibility and complexity of organic matter. Bioresource Technology. 10.1016/j.biortech.2017.01.057.

Mengel, K., 2007. Chapter 4: Potassium, in: Barker, A.V., Pilbeam, D.J. (Eds.), Handbook of Plant Nutrition. CRC Taylor & Francis, Boca Raton Fla. u.a., 481-511.

Möller, K., Müller, T., 2012. Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review. Engineering in Life Sciences 12, 242–257. 10.1002/elsc.201100085.

Möller, K., Schulz, R., Müller, T., 2010. Substrate inputs, nutrient flows and nitrogen loss of two centralized biogas plants in southern Germany. Nutrient Cycling in Agroecosystems 87, 307–325. 10.1007/s10705-009-9340-1.

Møller, H., 2000. Solid–liquid separation of livestock slurry: Efficiency and cost. Bioresource Technology 74, 223–229. 10.1016/S0960-8524(00)00016-X.

Møller, H.B., Sommer, S.G., Ahring, B.K., 2002. Separation efficiency and particle size distribution in relation to manure type and storage conditions. Bioresource Technology 85, 189–196. 10.1016/S0960-8524(02)00047-0.

Montag, D., Pinnekamp, J., Everding, W., Malms, S., Reinhardt, J., Fehrenbach, H., Arnold, U., Trimborn, M., Goldbach, H., Klett, W., Lammers, T., 2014. Bewertung konkreter Maßnahmen einer weitergehenden Phosphorrückgewinnung aus relevanten Stoffströmen sowie zum effizienten Phosphoreinsatz: Abschlussbericht. http://www.bmub.bund.de/fileadmin/Daten_BMU/Pools/Forschungsdatenbank/fkz_3713_26_301_phosphorrueckgewinnung_bf.pdf. Accessed 10 March 2018.

Müller, U., 2017. Aktuelle Entwicklungen zur Phosphorrückgewinnung. Landesamt für Umwelt, Landwirtschaft und Geologie Sachsen.

Nkoa, R., 2014. Agricultural benefits and environmental risks of soil fertilization with anaerobic digestates: A review. Agronomy for Sustainable Development 34, 473–492. 10.1007/s13593-013-0196-z.

Odlare, M., Arthurson, V., Pell, M., Svensson, K., Nehrenheim, E., Abubaker, J., 2011. Land application of organic waste – Effects on the soil ecosystem. Applied Energy 88, 2210–2218. 10.1016/j.apenergy.2010.12.043.

Odlare, M., Lindmark, J., Ericsson, A., Pell, M., 2015. Use of Organic Wastes in Agriculture. Energy Procedia 75, 2472–2476. 10.1016/j.egypro.2015.07.225.

Pavi, S., Kramer, L.E., Gomes, L.P., Miranda, L.A.S., 2017. Biogas production from co-digestion of organic fraction of municipal solid waste and fruit and vegetable waste. Bioresource Technology 228, 362–367. 10.1016/j.biortech.2017.01.003.

Pezzolla, D., Di Maria, F., Zadra, C., Massaccesi, L., Sordi, A., Gigliotti, G., 2017. Optimization of solid-state anaerobic digestion through the percolate recirculation. Biomass and Bioenergy 96, 112–118. 10.1016/j.biombioe.2016.11.012.

Pognani, M., Barrena, R., Font, X., Sánchez, A., 2012. A complete mass balance of a complex combined anaerobic/aerobic municipal source-separated waste treatment plant. Waste management (New York, N.Y.) 32, 799–805. 10.1016/j.wasman.2011.12.018.

Raussen, T., Kern, M., 2016. Optimale Aufbereitung von Gärresten aus der Bioabfallbehandlung: Ein Leitfaden.

Rehl, T., Müller, J., 2011. Life cycle assessment of biogas digestate processing technologies. Resources, Conservation and Recycling 56, 92–104. 10.1016/j.resconrec.2011.08.007.

Risberg, K., Cederlund, H., Pell, M., Arthurson, V., Schnürer, A., 2017. Comparative characterization of digestate versus pig slurry and cow manure - Chemical composition and effects on soil microbial activity. Waste management (New York, N.Y.) 61, 529–538. 10.1016/j.wasman.2016.12.016.

Rosenwinkel, K.-H., Kroiss, H., Dichtl, N., Seyfried, C.F., Weiland, P., 2015. Anaerobtechnik: Abwasser-, Schlamm- und Reststoffbehandlung, Biogasgewinnung, 3rd ed. Springer Vieweg, Berlin Germany, 1-111.

Rotter, S., 2002. Schwermetalle in Haushaltsabfällen: Potenzial, Verteilung und Steuerungsmöglichkeiten durch Aufbereitung. Zugl.: Dresden, Techn. Univ., Diss., 2002, Forum für Abfallwirtschaft und Altlasten e.V, Pirna.

Said-Pullicino, D., Erriquens, F.G., Gigliotti, G., 2007. Changes in the chemical characteristics of water-extractable organic matter during composting and their influence on compost stability and maturity. Bioresource Technology 98, 1822–1831. 10.1016/j.biortech.2006.06.018.

Sambusiti, C., Monlau, F., Ficara, E., Musatti, A., Rollini, M., Barakat, A., Malpei, F., 2015. Comparison of various post-treatments for recovering methane from agricultural digestate. Fuel Processing Technology 137, 359–365. 10.1016/j.fuproc.2015.04.028.

Saveyn, H., Eder, P., 2014. End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals. JRC Scientific and Policy Reports.

Schattauer, A., Abdoun, E., Weiland, P., Plöchl, M., Heiermann, M., 2011. Abundance of trace elements in demonstration biogas plants. Biosystems Engineering 108, 57–65. 10.1016/j.biosystemseng.2010.10.010.

Schaum, C., 2017. Technologien zur Rückgewinnung von Phosphor: Eine aktuelle Bestandsaufnahme. Universität München -

Siedlungswasserwirtschaft und Abfalltechnik. P-Rück Kongress - Ein kritischer Rohstoff mit Zukunft, 22 November 2017, Stuttgart.

Scholwin, F., Grope, J., Zacher, Rene, Nelles, Michael, 2013. Biogas aus Reststoffen und Abfall: Vermarktung von Biogas aus Reststoffen und Abfällen als Kraftstoff, zur Strom- und Wärmeproduktion, 21 November 2013, Dresden.

Schüch, A., Morscheck, G., Lemke, A., Nelles, M., 2016. Bio-waste Recycling in Germany – Further Challenges. Waste Management for Resource Utilisation 35, 308–318. 10.1016/j.proenv.2016.07.011.

Shao, Z.-H., He, P.-J., Zhang, D.-Q., Shao, L.-M., 2009. Characterization of water-extractable organic matter during the biostabilization of municipal solid waste. Journal of Hazardous Materials 164, 1191–1197. 10.1016/j.jhazmat.2008.09.035.

Smith, S.R., 2009. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environment International 35, 142–156. 10.1016/j.envint.2008.06.009.

Stoknes, K., Scholwin, F., Krzesiński, W., Wojciechowska, E., Jasińska, A., 2016. Efficiency of a novel "Food to waste to food" system including anaerobic digestion of food waste and cultivation of vegetables on digestate in a bubble-insulated greenhouse. Waste Management 56, 466–476. 10.1016/j.wasman.2016.06.027.

Stumm, W., Morgan, J.J., 1996. Aquatic chemistry: Chemical equilibria and rates in natural waters, 3rd ed. Wiley & Sons, New York NY u.a., XVI, 252-424.

Surendra, K.C., Takara, D., Hashimoto, A.G., Khanal, S.K., 2014. Biogas as a sustainable energy source for developing countries: Opportunities and challenges. Renewable and Sustainable Energy Reviews 31, 846–859. 10.1016/j.rser.2013.12.015.

Tambone, F., Genevini, P., D'Imporzano, G., Adani, F., 2009. Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW. Bioresource Technology 100, 3140–3142. 10.1016/j.biortech.2009.02.012.

Tambone, F., Orzi, V., D'Imporzano, G., Adani, F., 2017. Solid and liquid fractionation of digestate: Mass balance, chemical characterization, and agronomic and environmental value. Bioresource Technology 243, 1251–1256. 10.1016/j.biortech.2017.07.130.

Tambone, F., Scaglia, B., D'Imporzano, G., Schievano, A., Orzi, V., Salati, S., Adani, F., 2010. Assessing amendment and fertilizing properties of digestates from anaerobic digestion through a comparative study with digested sludge and compost. Chemosphere 81, 577–583. 10.1016/j.chemosphere.2010.08.034.

Tambone, F., Terruzzi, L., Scaglia, B., Adani, F., 2015. Composting of the solid fraction of digestate derived from pig slurry: Biological processes and compost properties. Waste management (New York, N.Y.) 35, 55–61. 10.1016/j.wasman.2014.10.014.

Tampio, E., Salo, T., Rintala, J., 2016. Agronomic characteristics of five different urban waste digestates. Journal of environmental management 169, 293–302. 10.1016/j.jenvman.2016.01.001.

Teglia, C., Tremier, A., Martel, J.-L., 2011a. Characterization of Solid Digestates: Part 2, Assessment of the Quality and Suitability for Composting of Six Digested Products. Waste Biomass Valor 2, 113–126. 10.1007/s12649-010-9059-x.

Teglia, C., Tremier, A., Martel, J.-L., 2011b. Characterization of Solid Digestates: Part 1, Review of Existing Indicators to Assess Solid Digestates Agricultural Use. Waste Biomass Valor 2, 43–58. 10.1007/s12649-010-9051-5.

Thygesen, O., Sommer, S.G., Shin, S.G., Triolo, J.M., 2014. Residual biochemical methane potential (BMP) of concentrated digestate from full-scale biogas plants. Fuel 132, 44–46. 10.1016/j.fuel.2014.04.062.

Tock, L., Schummer, J., 2017. Sustainable waste-to-value biogas plants for developing countries. Waste Management 64, 1–2. 10.1016/j.wasman.2017.05.014.

Veeken, A., Hamelers, B., 2002. Sources of Cd, Cu, Pb and Zn in biowaste. Science of The Total Environment 300, 87–98. 10.1016/S0048-9697(01)01103-2.

VDI (Verein Deutscher Ingenieure), 2006. Fermentation of organic materials - Characterisation of the substrate, sampling, collection of material data, fermentation tests. Beuth Verlag, Berlin.

Voelkner, A., Holthusen, D., Horn, R., 2015. Influence of homogenized residues of anaerobic digestate on the physicochemical properties of differently textured soils. Journal of Plant Nutrition and Soil Science 178, 261–269. 10.1002/jpln.201400138.

Walter, I., Martínez, F., Cala, V., 2006. Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses. Environmental Pollution 139, 507–514. 10.1016/j.envpol.2005.05.020.

Ward, A.J., Hobbs, P.J., Holliman, P.J., Jones, D.L., 2008. Optimisation of the anaerobic digestion of agricultural resources. Bioresource Technology 99, 7928–7940. 10.1016/j.biortech.2008.02.044.

Wei, Y., Zhao, Y., Xi, B., Wei, Z., Li, X., Cao, Z., 2015. Changes in phosphorus fractions during organic wastes composting from different sources. Bioresource Technology 189, 349–356. 10.1016/j.biortech.2015.04.031.

WEKA, 2015. Bioabfallverordnung (BioAbfV) wird neu gefasst.

Industrieverband Agrar e.V., 2017. Wichtige Zahlen Düngemittel: Produktion, Markt, Landwirtschaft.

http://www.iva.de/sites/default/files/benutzer/%25uid/publikationen/wichtige_zahlen_2016-2017.pdf. Accessed 18 January 2018.

Zeng, Y., Guardia, A. de, Dabert, P., 2016. Improving composting as a post-treatment of anaerobic digestate. Bioresource Technology 201, 293–303. 10.1016/j.biortech.2015.11.013.

Zhang, C., Su, H., Baeyens, J., Tan, T., 2014. Reviewing the anaerobic digestion of food waste for biogas production. Renewable and Sustainable Energy Reviews 38, 383–392. 10.1016/j.rser.2014.05.038.

Zirkler, D., Peters, A., Kaupenjohann, M., 2014. Elemental composition of biogas residues: Variability and alteration during anaerobic digestion. Biomass and Bioenergy 67, 89–98. 10.1016/j.biombioe.2014.04.021.

Zmora-Nahum, S., Markovitch, O., Tarchitzky, J., Chen, Y., 2005. Dissolved organic carbon (DOC) as a parameter of compost maturity. Soil Biology and Biochemistry 37, 2109–2116. 10.1016/j.soilbio.2005.03.013.

Appendix

Raw data for research paper 1 (section 4)

	Sample ID	Sample Nr	Day	pH	DM [%]	VS	C_{org} [g/kg DM]	N	P	K	Ca	Mg	S
MOW 1	M8in	68	0	5.4	33.4	77.4	380.9	16.6	1.8	8.8	19.8	2.5	2
	M8.1	72	2	4.9	19.2	73.2	353.5	29.9	2	16	20.1	2.8	1
	M8.2	73	4	5.7	19.9	72.5	383.2	19	2.6	15.8	21.6	2.5	4
	M8.3	74	7	5.9	17.5	69.7	359.2	16.5	2.6	18.5	25	2.7	3.3
	M8.4	75	9	6	13.5	70.8	392.3	19.1	2.1	22.9	20.3	2.7	6.8
	M8.5	76	11	6.3	14.1	74.5	392	15.9	1.4	20.9	18	2.4	2.8
	M8.6	77	14	6.5	15.1	73.8	394.3	18.4	1.5	24.3	21.9	2.5	2.2
	M8.7	78	16	6.9	16.9	67.9	420.4	17.5	1.4	20.1	20.6	2.3	5.3
	M8.8	79	18	7.5	20	67.8	353.6	18.2	1.9	19.5	27.5	2.9	3.9
	M8.9	80	21	7.6	13.1	73.1	398.5	18	1.7	28.7	21.7	2.5	3.7
	M8.10	81	23	7.6	16.8	69.2	391.7	18.6	1.6	23.4	19.7	2.2	3.4
	M8.11	82	25	8	11.3	72.4	411.9	18.4	1.4	24.2	21.3	2.5	6.8
	M8.12	83	28	7.9	17.3	68.6	352.3	19.8	1.8	24.9	24.2	3	10.4
	M8.13	84	30	7.9	16.3	66.5	355.7	17.9	1.4	23.8	26.8	2.9	6.7
	M8out	85	32	8.1	31.8	60.9	320.2	18.8	3.1	23.9	27	2.9	4.8
MOW 2	M12in	155	0	5.2	26.8	81.6	421.2	20.9	3	12.2	18.7	2.8	3.9
	M12.1	156	3	5.3	23	78	415.7	22.3	2.6	14.7	19.4	2.7	3.8
	M12.2	157	6	5.4	22.2	78.8	419.6	19.9	2.7	15	21	3	3.7
	M12.3	158	8	5.8	22.1	78.6	427.6	20.3	2.7	15.9	19.7	2.5	4.2
	M12.4	159	10	5.9	20.9	75.3	412.5	20.8	3.3	17.8	21.9	2.5	4.3
	M12.5	160	13	5.7	22.1	73.6	418.4	22.1	5.8	17.2	25.9	2.5	4.8
	M12.6	161	15	5.9	20.4	74.7	421.7	19.5	3.3	19.7	24.9	2.4	4.2
	M12.7	162	17	5.9	22.5	74	408.1	21.8	6.1	17.5	29.8	2.3	4.8
	M12.8	163	20	6.1	21.8	71.1	401.2	20.2	3	18.5	28.4	2.6	6.6
	M12.9	164	22	7.5	22.9	70.9	407.9	19.1	4.1	19.8	31.5	2.9	5
	M12out	165	27	7.3	25.3	68.1	384.5	21.3	4.3	18.3	32.1	3.2	4.6
MOW 3	M14in	226	0	4.9	31.6	72.4	359.9	17.7	3.1	11.1	20.9	1.3	4.8
	M14.1	229	2	5.1	27.1	50.6	343.9	19.6	2.6	15.9	23.8	1.2	4.4
	M14.2	230	5	6.8	24.2	68.9	339.9	14.3	2.4	18.5	24.2	1.1	5.7
	M14.3	231	8	6.2	29.7	49	273.8	15.9	2.3	14.6	36.9	1.3	4.8
	M14.4	232	13	6.1	29.4	58.7	nd	17.5	2.1	13.2	16.3	3	4.7
	M14.5	233	17	5.9	27.5	57.8	305.6	15	2.6	14.3	25.5	2.8	5
	M14.6	234	20	6.7	28.1	59	335.9	18.9	5.9	14.7	27.5	3.3	4.8
	M14out	235	28	7.5	28.6	51	283.1	19.4	3.5	16.4	23.5	3.1	6.2

	Sample ID	Sample Nr	Day	Cd [mg/kg DM]	Cr [mg/kg DM]	Cu [mg/kg DM]	Ni [mg/kg DM]	Pb [mg/kg DM]	Zn [mg/kg DM]
MOW 1	M8in	68	0	0.8	13.2	20	6.5	32.4	129.7
	M8.1	72	2	1.1	15.2	28.6	7.4	41.2	156.5
	M8.2	73	4	0.8	14.4	27.8	8.7	34.1	124.9
	M8.3	74	7	1	20.4	35.5	8.6	66.1	159.3
	M8.4	75	9	0.9	16.9	38.9	9.2	42.7	156.9
	M8.5	76	11	0.9	14.7	44.3	7.9	36.1	151.7
	M8.6	77	14	1.1	16.2	75.1	9.4	51.3	198.7
	M8.7	78	16	1	15.8	76.9	9.9	39	187.7
	M8.8	79	18	1.1	18.1	42.5	10.3	45.3	206.5
	M8.9	80	21	0.9	18.9	37.2	11.1	53.4	175.4
	M8.10	81	23	1.1	20.5	39.3	10.7	49	194.5
	M8.11	82	25	1.1	19.4	53.3	11.1	44.6	215.4
	M8.12	83	28	1.6	18.3	59.9	10.4	49	208.6
	M8.13	84	30	nd	nd	nd	nd	nd	nd
	M8out	85	32	1.1	20.2	40.4	11	43.1	185
MOW 2	M12in	155	0	0.7	12.2	19.5	7.1	49.2	206.8
	M12.1	156	3	0.9	14.7	37	8.4	58.9	227.1
	M12.2	157	6	0.9	15.3	27.1	11.5	50.5	215.8
	M12.3	158	8	0.8	15.7	30.6	8.5	61.2	212
	M12.4	159	10	0.9	15.5	47.6	9	64.3	244.3
	M12.5	160	13	1	18.2	75	10.7	82.6	293.4
	M12.6	161	15	0.8	16.5	43.7	8.9	67.5	257.1
	M12.7	162	17	1.8	16.7	52.2	9.8	72.7	313.9
	M12.8	163	20	1	17.8	59.7	11.9	81.6	295
	M12.9	164	22	0.9	22.4	47.7	13.3	76.5	286.8
	M12out	165	27	1.1	24.1	67.4	14.5	83.3	318.9
MOW 3	M14in	226	0	1.8	18.9	46.6	9.9	188.8	343.4
	M14.1	229	2	1.5	16	84.2	10.5	281.7	343.7
	M14.2	230	5	1.4	17.8	142.5	10.6	164.2	482
	M14.3	231	8	1.5	23.4	169.8	12.7	195.3	425.1
	M14.4	232	13	1.7	27.3	71.9	11.3	171.8	352.9
	M14.5	233	17	2.9	21.2	128.2	11.6	261	494.8
	M14.6	234	20	2	26.6	107.7	11.9	231.4	479.6
	M14out	235	28	2.1	24.2	117	13.3	262	470.3

	MOW 1	MOW 2	MOW 3
Input [kg DM]	17.4	12.7	16.5
Output [kg DM]	6.6	5.4	8.1
Sampling [kg DM]	4.4	2.4	1.6
Number of samples	13	9	6

Day	Sample-ID	Biogas yield [Nl/kg VS]	MP [Nl/kg VS]
0	M 8in	647.3	406.3
		714.1	450.9
		593.6	371.6
2	M 8.1	524.8	340.9
		560.9	366.4
4	M 8.2	660.8	441.9
		707.9	472.3
7	M 8.3	488.8	343.7
		407.5	291
9	M 8.4	638.1	442.3
		564	410.8
11	M 8.5	437.1	329.1
		447.4	337.3
14	M 8.6	378.2	285.7
		410.9	309.6
16	M 8.7	326.2	247.8
		336.7	261.4
18	M 8.8	398.8	294
		405.7	290.6
21	M 8.9	366.9	278.4
		306	246.9
23	M 8.10	337.4	274.2
		332.7	268.6
25	M 8.11	485.8	384.5
		440.4	349
28	M 8.12	272.5	219.9
		267.6	218.5
30	M 8.13	298.5	246.9
		287.9	238.5
32	M 8out	104.4	94.6
		104.5	90.1

Day	Sample-ID	Biogas yield [Nl/kg VS]	MP [Nl/kg VS]
0	M 12in	677.4	412.2
		667.5	422
		629	395.5
3	M 12.1	601.7	413.5
		643.2	433.5
6	M 12.2	634.2	430.7
		665.5	452.3
8	M 12.3	590.1	421
		547.6	385.5
10	M 12.4	657.3	463.1
		685.3	463.3
13	M 12.5	660.8	463.4
		647.6	455.2
15	M 12.6	657.9	470.4
		670.4	481
17	M 12.7	601.4	433.7
		566.8	410.8
20	M 12.8	629.6	448.3
		556.4	405.8
22	M 12.9	489.2	381.3
		472.1	367.5
27	M 12out	453.7	356.4
		433.7	336.8

Day	Sample-ID	Biogas yield [Nl/kg VS]	MP [Nl/kg VS]
0	M 14in	535.4	315.3
		531.9	316.2
2	M 14.1	610.3	379
		589	367.5
5	M 14.2	406.7	281.2
		370.8	260
8	M 14.3	593.6	405.8
		543.5	383.6
13	M 14.4	328.4	251.9
		319.6	242.6
17	M 14.5	315.8	246.8
		317.4	248.1
20	M 14.6	318.3	252.4
		393.1	310.4
28	M 14.7	307.9	251.3
		341	266.8
36	M 14out	224.6	188.6
		195.6	168.3

Raw data for research paper 2 (section 5)

Sample ID	Sample Nr.	Sample weigth [g]	0,01 M $CaCl_2$ Solution [ml]	Result N_{pa} [mg/l]	DM	N_{pa} [g/kg DM]
$D1_{fresh}$	251-1	20	200	103.2	33.7	3.3
	251-2	20	200	107.4		
$D1_{oven}$	252-1	20	200	142.4	99.1	1.5
	252-2	20	200	150.8		
$D1_{air}$	253-1	20	200	116.0	98.2	1.3
	253-2	20	200	136.7		
$D2_{fresh}$	254-1	20	200	115.0	29.8	4.0
	254-2	20	200	109.2		
$D2_{oven}$	255-1	20	200	101.3	99.1	1.0
	255-2	20	200	92.3		
$D2_{air}$	256-1	20	200	172.0	95.9	1.7
	256-2	20	200	161.1		
$D3_{oven}$	260-1	20	200	103.3	99.2	1.0
	260-2	20	200	102.5		
$D3_{air}$	261-1	20	200	70.9	97.4	0.7
	261-2	20	200	74.7		
$D3_{fresh}$	262-1	20	200	120.9	32.7	3.9
	262-2	20	200	117.2		
$D1_{comp}$	272-1	20	200	19.9	50.6	0.4
	272-2	20	200	20.9		
$D2_{comp}$	274-1	20	200	35.2	48.8	0.7
	274-2	20	200	33.2		
$D3_{comp}$	276-1	20	200	31.3	51.5	0.6
	276-2	20	200	32.0		

Sample ID	Sample Nr.	Sample weigth [g]	0,01 M CAL Solution [ml]	Result P_{pa} [mg/l]	DM	P_{pa} [g/kg DM]
$D1_{fresh}$	251-1	20	400	13.4	33.7	0.8
	251-2	20	400	13.2		
$D1_{oven}$	252-1	20	400	30.6	99.1	0.6
	252-2	20	400	30.3		
$D1_{air}$	253-1	20	400	25.8	98.2	0.5
	253-2	20	400	28.0		
$D2_{fresh}$	254-1	20	400	14.6	29.8	1.0
	254-2	20	400	15.2		
$D2_{oven}$	255-1	20	400	38.4	99.1	0.7
	255-2	20	400	31.6		
$D2_{air}$	256-1	20	400	35.9	95.9	0.7
	256-2	20	400	33.5		
$D3_{oven}$	260-1	20	400	46.0	99.2	0.9
	260-2	20	400	45.0		
$D3_{air}$	261-1	20	400	31.5	97.4	0.7
	261-2	20	400	36.4		
$D3_{fresh}$	262-1	20	400	21.7	32.7	1.2
	262-2	20	400	18.1		
$D1_{comp}$	272-1	20	400	25.9	50.6	1.1
	272-2	20	400	29.3		
$D2_{comp}$	274-1	20	400	29.4	48.8	1.2
	274-2	20	400	29.9		
$D3_{comp}$	276-1	20	400	33.6	51.5	1.3
	276-2	20	400	31.9		

Sample ID	Sample Nr.	Sample weigth [g]	0,01 M CAL Solution [ml]	Result K_{pa} [mg/l]	DM	K_{pa} [g/kg DM]
$D1_{fresh}$	251-1	20	400	93.1	33.7	5.5
	251-2	20	400	93.1		
$D1_{oven}$	252-1	20	400	265.7	99.1	5.3
	252-2	20	400	261.2		
$D1_{air}$	253-1	20	400	234.8	98.2	4.7
	253-2	20	400	228.8		
$D2_{fresh}$	254-1	20	400	79.9	29.8	5.4
	254-2	20	400	79.8		
$D2_{oven}$	255-1	20	400	231.3	99.1	4.8
	255-2	20	400	240.6		
$D2_{air}$	256-1	20	400	224.1	95.9	4.6
	256-2	20	400	217.6		
$D3_{oven}$	260-1	20	400	315.7	99.2	6.2
	260-2	20	400	300.9		
$D3_{air}$	261-1	20	400	268.8	97.4	5.7
	261-2	20	400	286.5		
$D3_{fresh}$	262-1	20	400	96.5	32.7	6.0
	262-2	20	400	98.9		
$D1_{comp}$	272-1	20	400	136.1	50.6	5.6
	272-2	20	400	145.3		
$D2_{comp}$	274-1	20	400	133.3	48.8	5.4
	274-2	20	400	129.8		
$D3_{comp}$	276-1	20	400	173.6	51.5	6.7
	276-2	20	400	170.0		

Sample ID	Sample Nr.	Sample weigth [g FM]	$MgSO_4$ solution [ml]	Result Mg [mg/l]	Mg used [mg]	Mg used in cmol/ kg DM = CEC
$D1_{oven}$	252-1	5.00	50.58	183.8	13.8	23.1
	252-2	5.02	51.05	179.6	14.2	23.7
$D1_{air}$	253-1	5.03	50.91	174.8	14.4	24.1
	253-2	5.00	50.67	182.8	13.9	23.4
$D2_{oven}$	255-1	5.01	50.80	178.1	14.2	23.9
	255-2	5.00	50.59	178.1	14.2	23.8
$D2_{air}$	256-1	5.00	50.83	195.4	13.0	21.9
	256-2	5.00	50.35	213.9	11.7	19.7
$D3_{oven}$	261-1	5.01	50.58	196.9	12.8	21.4
	261-2	5.01	50.69	195.4	12.9	21.5
$D1_{comp}$	272-1	5.00	50.24	114	18.0	30.1
	272-2	5.01	50.23	119.5	17.6	29.5
$D2_{comp}$	274-1	5.01	50.87	126.4	17.2	28.8
	274-2	5.00	50.68	114.2	18.0	30.2
$D3_{comp}$	276-1	5.00	50.79	136.2	16.7	28.1
	276-2	5.01	50.75	148.4	16.0	26.8

Sample ID	Sample Nr.	Sample weight [g DM]	Solution [ml]	Result Ca [mg/l]	Ca elution [g/kg DM]	Result K [mg/l]	K elution [g/kg DM]	Result Mg [mg/l]	Mg elution [g/kg DM]	Result P [mg/l]	P elution [g/kg DM]	Result DOC [mg/l]	DOC elution [g/kg DM]	pH
$D1_{air}$	RS13	85.46	905.58	147.7	1.57	317.3	3.36	41.47	0.44	11.79	0.12	1455	15.42	6.22
	RS14	85.53	905.53	176.5	1.87	335.2	3.55	47.58	0.5	13.58	0.14	1696	17.96	6.02
	RS15	85.44	907.54	156.2	1.66	354.3	3.76	43.42	0.46	13.63	0.14	1586	16.85	6.15
	RS16	85.49	905.6	168.4	1.78	347.7	3.68	46.05	0.49	13.38	0.14	1599	16.94	6.18
$D1_{oven}$	RS17	86.92	903.64	167.3	1.74	315	3.27	42.51	0.44	13.6	0.14	1791	18.62	5.9
	RS18	86.68	906.1	156.6	1.64	313.7	3.28	40.1	0.42	13.77	0.14	1663	17.38	5.94
	RS19	86.82	908.69	154.1	1.61	314.9	3.3	39.53	0.41	14.25	0.15	1765	18.47	5.91
	RS20	86.94	904.59	172.7	1.8	324.3	3.37	42.38	0.44	14.82	0.15	1799	18.72	5.95
$D1_{comp}$	RS21	80.96	913.27	46.67	0.53	218.9	2.47	8.15	0.09	8.35	0.09	189	2.13	7.22
	RS22	80.93	914	34.7	0.39	223.2	2.52	7.93	0.09	8.28	0.09	187	2.11	7.21
	RS23	80.96	911.99	38.49	0.43	236.7	2.67	8.9	0.1	9.16	0.1	203	2.29	7.14
	RS24	80.95	912.73	36.91	0.42	234.6	2.65	8.38	0.09	7.36	0.08	200	2.26	7.15
$D2_{air}$	7-1	92.11	898.24	188.6	1.84	435.7	4.25	55.74	0.54	13.76	0.13	1597	15.57	6.24
	7-2	92.04	899.93	165.9	1.62	423.3	4.14	50	0.49	13.71	0.13	1423	13.91	6.39
	7-3	92.04	898.85	207.5	2.03	499.3	4.88	58.27	0.57	14.88	0.15	1689	16.49	6.36
	7-4	91.84	898.77	184.7	1.81	459.6	4.5	52.57	0.51	13.76	0.13	1527	14.94	6.41
$D2_{oven}$	8-1	92.91	898.06	125.2	1.21	456.5	4.41	42.37	0.41	19.3	0.19	1419	13.72	6.36
	8-2	93.12	897.97	93.38	0.9	406.4	3.92	33.49	0.32	18.87	0.18	1240	11.96	6.36
	8-3	93.33	897.84	82.84	0.8	383.9	3.69	29.63	0.29	17.64	0.17	1135	10.92	6.4
	8-4	92.97	898.53	88.71	0.86	399.4	3.86	32.25	0.31	19.17	0.19	1192	11.52	6.35
$D2_{comp}$	9-1	88.46	901.92	63.94	0.65	290.3	2.96	13.24	0.13	4.65	0.05	84.92	0.87	7.36
	9-2	88.55	903.32	52.44	0.53	301.2	3.07	14.18	0.14	5.34	0.05	99.86	1.02	7.41
	9-3	88.86	909.85	56.98	0.58	296.6	3.04	14.27	0.15	15.73	0.16	91.8	0.94	7.41
	9-4	88.48	901.82	50.55	0.52	298.2	3.04	13.78	0.14	5.41	0.06	95.96	0.98	7.4
$D3_{air}$	10-1	93.41	897.6	89.81	0.86	505	4.85	38.31	0.37	29.41	0.28	1034	9.94	6.76
	10-2	93.47	898.78	116.1	1.12	512.5	4.93	44.24	0.43	25.01	0.24	1141	10.97	6.74
	10-3	93.45	897.61	113.2	1.09	484.8	4.66	37.9	0.36	25.84	0.25	1091	10.48	6.72
	10-4	93.85	897.43	118.2	1.13	506.9	4.85	44.87	0.43	24.37	0.23	1152	11.02	6.75
$D3_{oven}$	11-1	93.04	898.5	83.7	0.81	489.1	4.72	31.33	0.3	26.5	0.26	1082	10.45	6.54
	11-2	93.02	897.25	82.62	0.8	503	4.85	31.65	0.31	28.46	0.27	1130	10.9	6.71
	11-3	93.15	897.29	85.22	0.82	493.8	4.76	32.3	0.31	25.18	0.24	1078	10.38	6.69
	11-4	93.47	897.37	83.24	0.8	501.7	4.82	32.27	0.31	27.55	0.26	1070	10.27	6.61
$D3_{comp}$	12-1	94.06	897.62	74.19	0.71	458.8	4.38	20.06	0.19	13.91	0.13	156.8	1.5	7.25
	12-2	93.46	897.18	77.28	0.74	466.4	4.48	22.11	0.21	14.5	0.14	153.4	1.47	7.33
	12-3	93.52	899.1	70.18	0.67	446.9	4.3	18.97	0.18	13.09	0.13	150.1	1.44	7.35
	12-4	93.72	897.54	72.7	0.7	448.6	4.3	19.6	0.19	14.21	0.14	155.2	1.49	7.37

Sample ID	Sample Nr.	Sample weight [g DM]	Solution [ml]	Result Cd [mg/l]	Cd elution [mg/kg DM]	Result Cr [mg/l]	Cr elution [mg/kg DM]	Result Cu [mg/l]	Cu elution [mg/kg DM]	Result Ni [mg/l]	Ni elution [mg/kg DM]	Result Pb [mg/l]	Pb elution [mg/kg DM]	Result Zn [mg/l]	Zn elution [mg/kg DM]
$D1_{air}$	RS13	85.46	905.6	0.0005	0.005	0.01	0.07	0.14	1.48	0.08	0.85	0.04	0.46	0.34	3.58
	RS14	85.53	905.5	0.0004	0.004	0.01	0.14	0.12	1.31	0.08	0.89	0.06	0.65	0.4	4.22
	RS15	85.44	907.5	0.0006	0.006	0.01	0.08	0.26	2.79	0.08	0.86	0.03	0.35	0.38	4
	RS16	85.49	905.6	0.0004	0.004	0.02	0.2	0.1	1.02	0.08	0.87	0.06	0.62	0.37	3.89
$D1_{oven}$	RS17	86.92	903.6	0.0009	0.009	0.01	0.09	0.13	1.31	0.07	0.78	0.06	0.67	0.47	4.92
	RS18	86.68	906.1	0.0009	0.009	0.01	0.08	0.11	1.19	0.07	0.75	0.07	0.71	0.48	4.97
	RS19	86.82	908.7	0.0012	0.013	0.01	0.08	0.14	1.45	0.07	0.78	0.08	0.78	0.48	5.03
	RS20	86.94	904.6	0.001	0.01	0.03	0.26	0.18	1.85	0.08	0.85	0.08	0.85	0.49	5.09
$D1_{comp}$	RS21	80.96	913.3	0.0009	0.01	0.01	0.07	0.16	1.77	0.03	0.36	0.08	0.94	0.23	2.62
	RS22	80.93	914	0.0007	0.008	0.01	0.07	0.12	1.35	0.03	0.36	0.07	0.78	0.22	2.43
	RS23	80.96	912	0.0014	0.016	0.01	0.07	0.13	1.43	0.03	0.37	0.13	1.49	0.21	2.39
	RS24	80.95	912.7	0.0007	0.008	0.01	0.08	0.1	1.17	0.03	0.33	0.09	0.99	0.18	2.05
$D2_{air}$	7-1	92.11	898.2	0.0004	0.004	0.01	0.1	0.1	0.98	0.1	0.98	0.02	0.2	0.47	4.62
	7-2	92.04	899.9	0.0007	0.007	0.01	0.11	0.09	0.84	0.1	0.96	0.05	0.49	0.37	3.64
	7-3	92.04	898.9	0.0007	0.007	0.01	0.12	0.08	0.76	0.1	0.96	0.05	0.53	0.48	4.68
	7-4	91.84	898.8	0.0001	0.001	0.01	0.11	0.07	0.67	0.1	0.94	0.08	0.77	0.41	4.01
$D2_{oven}$	8-1	92.91	898.1	0.0002	0.002	0.01	0.11	0.1	0.99	0.13	1.27	0.05	0.53	0.46	4.47
	8-2	93.12	898	0.0003	0.003	0.01	0.13	0.16	1.51	0.15	1.41	0.02	0.21	0.45	4.31
	8-3	93.33	897.8	0.0003	0.003	0.01	0.1	0.19	1.79	0.12	1.16	0.02	0.24	0.48	4.6
	8-4	92.97	898.5	0.0003	0.003	0.01	0.11	0.1	0.92	0.13	1.21	0.04	0.4	0.41	3.96
$D2_{comp}$	9-1	88.46	901.9	0.0003	0.003	0	0.04	0.08	0.8	0.05	0.46	< 0.01	0	0.1	1.04
	9-2	88.55	903.3	0.0002	0.002	0	0.04	0.06	0.56	0.04	0.43	< 0.01	0	0.1	0.98
	9-3	88.86	909.9	0.0005	0.005	0	0.04	0.06	0.62	0.04	0.42	< 0.01	0	0.12	1.25
	9-4	88.48	901.8	0.0002	0.002	0	0.03	0.06	0.63	0.04	0.39	< 0.01	0	0.09	0.91
$D3_{air}$	10-1	93.41	897.6	0.0001	0.001	0.01	0.1	0.1	0.93	0.08	0.78	0.1	0.99	0.17	1.62
	10-2	93.47	898.8	< 0.00009	0	0.01	0.1	0.07	0.7	0.08	0.79	0.08	0.75	0.17	1.68
	10-3	93.45	897.6	0.0001	0.001	0.01	0.11	0.06	0.56	0.09	0.84	0.06	0.55	0.16	1.52
	10-4	93.85	897.4	< 0.00009	0	0.01	0.11	0.05	0.48	0.09	0.81	0.07	0.67	0.2	1.91
$D3_{oven}$	11-1	93.04	898.5	0.0016	0.016	0.01	0.13	0.19	1.8	0.1	1.01	0.09	0.88	0.45	4.34
	11-2	93.02	897.3	0.0021	0.02	0.02	0.15	0.22	2.08	0.11	1.05	0.1	0.94	0.4	3.89
	11-3	93.15	897.3	0.0015	0.014	0.01	0.13	0.17	1.66	0.1	0.96	0.1	0.96	0.39	3.72
	11-4	93.47	897.4	0.0024	0.023	0.02	0.16	0.52	5.01	0.1	0.94	0.17	1.62	0.69	6.64
$D3_{comp}$	12-1	94.06	897.6	0.0012	0.012	0.01	0.08	0.09	0.85	0.04	0.34	0.05	0.45	0.18	1.76
	12-2	93.46	897.2	0.0014	0.013	0.01	0.12	0.11	1.06	0.04	0.4	0.08	0.78	0.24	2.28
	12-3	93.52	899.1	0.0011	0.011	0.01	0.06	0.1	0.99	0.04	0.35	< 0.01	0	0.23	2.23
	12-4	93.72	897.5	0.0011	0.011	0.01	0.09	0.09	0.88	0.04	0.36	0.06	0.58	0.21	2.04

Sample ID	Sample Nr.	Sample weight [g DM]	Solution [ml]	Result Cd [mg/l]	Cd elution [mg/kg DM]	Result Cr [mg/l]	Cr elution [mg/kg DM]	Result Cu [mg/l]	Cu elution [mg/kg DM]	Result Ni [mg/l]	Ni elution [mg/kg DM]	Result Pb [mg/l]	Pb elution [mg/kg DM]	Result Zn [mg/l]	Zn elution [mg/kg DM]
D1air	RS.3	85.5	905.6	0.0005	0.0053	0.0063	0.0668	0.14	1.48	0.08	0.85	0.04	0.46	0.34	3.58
	RS.4	85.5	905.3	0.0004	0.0042	0.0135	0.1429	0.12	1.31	0.08	0.89	0.06	0.65	0.40	4.22
	RS.5	85.4	907.3	0.0005	0.0064	0.0074	0.0786	0.26	2.79	0.08	0.86	0.03	0.35	0.38	4.00
	RS.6	85.5	905.6	0.0004	0.0042	0.0185	0.156	0.10	1.02	0.08	0.87	0.06	0.62	0.37	3.89
D1even	RS.7	86.9	903.6	0.0009	0.0094	0.0082	0.0853	0.13	1.31	0.07	0.78	0.06	0.67	0.47	4.92
	RS.8	86.7	906.1	0.0009	0.0094	0.0075	0.0784	0.11	1.19	0.07	0.75	0.07	0.71	0.48	4.97
	RS.9	86.8	908.7	0.0012	0.0126	0.0072	0.0754	0.14	1.45	0.07	0.78	0.08	0.78	0.48	5.03
	RS0	86.9	904.6	0.001	0.0104	0.0253	0.2632	0.18	1.85	0.08	0.85	0.08	0.85	0.49	5.09
D1comp	RS1	81.0	913.3	0.0009	0.0102	0.0059	0.0656	0.16	1.77	0.03	0.36	0.08	0.94	0.23	2.62
	RS2	86.9	914.0	0.0007	0.0075	0.0061	0.0689	0.12	1.35	0.03	0.36	0.07	0.78	0.22	2.43
	RS3	81.0	912.0	0.0014	0.0158	0.0063	0.071	0.13	1.43	0.03	0.37	0.13	1.49	0.21	2.39
	RS4	81.0	912.7	0.0007	0.0075	0.0075	0.0846	0.10	1.17	0.03	0.33	0.09	0.99	0.18	2.05
D2air	7-1	92.1	898.2	0.0004	0.0035	0.0104	0.1014	0.10	0.98	0.10	0.98	0.02	0.20	0.47	4.62
	7-2	92.0	899.9	0.0007	0.0068	0.0109	0.1056	0.09	0.84	0.10	0.96	0.05	0.49	0.37	3.64
	7-3	92.0	898.9	0.0007	0.0068	0.0121	0.1182	0.08	0.76	0.10	0.96	0.05	0.53	0.48	4.68
	7-4	91.8	898.8	0.001	0.001	0.0108	0.1057	0.07	0.67	0.10	0.94	0.08	0.77	0.41	4.01
D2even	8-1	92.9	898.1	0.0002	0.0019	0.0113	0.1092	0.10	0.99	0.13	1.27	0.05	0.53	0.46	4.47
	8-2	93.1	898.0	0.0003	0.0025	0.0138	0.1331	0.16	1.51	0.15	1.41	0.02	0.21	0.45	4.31
	8-3	93.3	897.8	0.0003	0.0025	0.0106	0.102	0.19	1.79	0.12	1.16	0.02	0.24	0.48	4.60
	8-4	93.0	898.5	0.0003	0.0029	0.0113	0.1092	0.10	0.92	0.13	1.21	0.04	0.40	0.41	3.96
D2comp	9-1	88.5	901.9	0.0003	0.0031	0.0044	0.0449	0.08	0.80	0.05	0.46	<0.01	0.00	0.10	1.04
	9-2	88.6	903.3	0.0002	0.002	0.0044	0.0449	0.06	0.56	0.04	0.43	<0.01	0.00	0.10	0.98
	9-3	88.9	909.9	0.0005	0.0051	0.0041	0.042	0.06	0.62	0.04	0.42	<0.01	0.00	0.12	1.25
	9-4	88.5	901.8	0.0002	0.002	0.003	0.0306	0.06	0.63	0.04	0.39	<0.01	0.00	0.09	0.91
D3air	10-1	93.4	897.6	0.0001	0.001	0.01	0.0951	0.10	0.93	0.08	0.78	0.10	0.99	0.17	1.62
	10-2	93.5	898.8	<0.00009	9	0.0104	0.1	0.07	0.70	0.08	0.79	0.08	0.75	0.17	1.68
	10-3	93.5	897.6	0.0001	0.001	0.0113	0.1085	0.06	0.56	0.09	0.84	0.06	0.55	0.16	1.52
	10-4	93.9	897.4	<0.00009	9	0.0115	0.11	0.05	0.48	0.09	0.81	0.07	0.67	0.20	1.91
D3even	11-1	93.0	898.5	0.0015	0.0155	0.013	0.1255	0.19	1.80	0.10	1.01	0.09	0.88	0.45	4.34
	11-2	93.0	897.3	0.0021	0.0203	0.0157	0.1514	0.22	2.08	0.11	1.05	0.10	0.94	0.40	3.89
	11-3	93.2	897.3	0.0015	0.0144	0.0137	0.132	0.17	1.66	0.10	0.96	0.10	0.96	0.39	3.72
	11-4	93.5	897.4	0.0024	0.023	0.0164	0.1575	0.52	5.01	0.10	0.94	0.17	1.62	0.69	6.64
D3comp	12-1	94.1	897.6	0.0012	0.0115	0.0079	0.0754	0.09	0.85	0.04	0.34	0.05	0.45	0.18	1.76
	12-2	93.5	897.2	0.0014	0.0134	0.0122	0.1171	0.11	1.06	0.04	0.40	0.08	0.78	0.24	2.28
	12-3	93.5	899.1	0.0011	0.0106	0.0066	0.0635	0.10	0.99	0.04	0.35	<0.01	0.00	0.23	2.23
	12-4	93.7	897.5	0.0011	0.0105	0.0098	0.0939	0.09	0.88	0.04	0.36	0.06	0.58	0.21	2.04

$D_{comp}4$

Size fraction	Weight of fraction [kg DM]	Cummulative weight [kg DM]	Cd [mg/kg DM]	Cr [mg/kg DM]	Cu [mg/kg DM]	Ni [mg/kg DM]	Pb [mg/kg DM]	Zn [mg/kg DM]
< 0.5 mm	2.5	2.5	2.34	49.04	83.89	26.39	209.9	603.8
< 1mm	1.7	4.3	2.93	45.08	87.49	25.67	214.6	634.6
< 2mm	3.7	8	2.32	37.08	74.86	23.01	194.1	557.6
< 5 mm	4.7	12.6	2.01	38.26	66.76	23.63	179.3	493.25
< 10 mm	6.7	19.3	2.03	44.01	47.6	23.47	98.58	316.44
< 20 mm	8.2	**27.5**	2.07	43.79	57.07	20.28	94.79	374.51

$D_{comp}5$

Size fraction	Weight of fraction [kg DM]	Cummulative weight [kg DM]	Cd [mg/kg DM]	Cr [mg/kg DM]	Cu [mg/kg DM]	Ni [mg/kg DM]	Pb [mg/kg DM]	Zn [mg/kg DM]
< 0.5 mm	1.8	1.8	3.73	32.18	140.2	23.66	177.6	628
< 1mm	1.5	3.3	4.65	30.99	106	29.98	186.2	653.6
< 2mm	1.5	4.8	2.9	29.64	115.5	21.17	156.8	532.7
< 5 mm	3.9	8.7	2.98	27.6	96.38	19.05	150.25	481.05
< 10 mm	5.3	14	2.53	26.81	95.53	29.86	128	519
< 20 mm	6.2	**20.2**	2.41	23.47	79.58	15.99	118.7	446

$D_{comp}6$

Size fraction	Weight fraction [kg DM]	Cummulative weight [kg DM]	Cd [mg/kg DM]	Cr [mg/kg DM]	Cu [mg/kg DM]	Ni [mg/kg DM]	Pb [mg/kg DM]	Zn [mg/kg DM]
< 5 mm	11.1	11.1	0.68	28.95	47.14	15.9	135.8	341.9
< 10 mm	4.6	15.7	0.78	28.16	52.71	15.71	78.67	358.3
< 20 mm	5.2	**21**	0.62	25.33	52.56	14.54	94.91	338.1

Raw data for research paper 3 (section 6)

Sample ID		Input [t]	Output [t]
Batch 1	HY1	6.04	5.09
	HY2	6.52	5.7
Batch 2	HY1	6.22	5.84
	HY2	7.08	6.5
Batch 3	HY1	12.68	12.68
	HY2		
Batch 4	HY1	14.94	10.28
	HY2		
Batch 5	HY1	14.16	12.14
	HY2		
Batch 6	HY1	17.2	16.92
	HY2		
Batch 7	HY1	6.67	4.44
	HY2	6.67	4.48
Batch 8	HY1	6.12	5.1
	HY2	7.93	6
Batch 9	HY1	6.15	5.62
	HY2	6.69	5.96
Batch 10	HY1	5.94	5.2
	HY2	5.86	4.96
Batch 11	HY1	6.1	4.92
	HY2	5.55	4.72
Batch 12	HY1	5.77	5.44
	HY2	5.85	4.84
Batch 13	HY1	6.78	6.32
	HY2	6.22	5.46
Batch 14	HY1	6.17	5
	HY2	6.25	4.48
Batch 15	HY1	7.34	6.68
	HY2	6.87	5.92

			g/kg DM						mg/kg DM						%					
	Sample Nr	Sample ID	N	P	K	Mg	Ca	S	Cd	Cr	Cu	Ni	Pb	Zn	DM	VS	C	pH	SAL	NH_4
MOW	1	BA2 216	24.2	3.3	10.2	1.1	34.8	6	2.2	14.8	42.9	10.1	52.7	309.4	27.3	82.6	44.6	4.5	1.7	6.7
	2	BA3 218	23	10.1	11.2	1.2	43.3	4.9	0.5	17.7	32.8	11.2	48.4	176.1	29.7	81.2	42	5	1.2	5
	3	BA4 226	18.3	3.1	10.4	1.3	20.3	4.4	2	20.4	47.5	11.4	211.2	363.1	32.4	70.9	35.8	4.9	1.3	4.6
	4	BA5 237	21.2	3.7	21	4.7	28.3	5.4	3.4	25.5	144.9	14.4	336.8	635.9	32.4	74.6	38.1	4.9	1.1	3.6
	5	BA6 245	21.9	4.1	11.4	3	20.5	5.1	1.6	16.3	45.4	7	153.4	359.9	31.7	75	38.2	4.6	1.6	5.6
	6	BA7 277	19.1	3.9	11.5	2.7	24.5	6	1.4	22.3	64.4	10.3	127.8	294.5	29.9	75	39.5	4.3	1.3	4.7
	7	BA8 291	20.4	3.9	9.9	2.1	26.8	6.8	0.9	6.7	27.7	2.5	82.7	212	30.7	80.6	42.1	4.8	1.1	5.9
	8	BA9 295	17.4	3.4	10.3	2.7	25.6	6.1	1.1	13.7	32.2	5.8	82.5	351.7	35.5	78.3	40.4	5.1	0.9	3.2
	9	BA10 313	17.1	2.7	10	2.1	20.1	5.4	0.7	7.5	22	2.8	50.2	196.7	30.6	82.7	40.8	4.6	0.9	2.5
	10	BA 11 314	18.9	3	10.1	2.4	22.7	5.2	0.3	5.6	15.3	2.6	24.6	124.8	31.6	82.8	44.3	5.2	0.8	3.5
MOW + Bulk material	1	V00 -	15.7	2.1	9.5	nd	nd	4.3	0.6	10.8	15.6	6	34.3	142.5	34	82.9	39.1			
	2	V3 -	18.7	1.5	8.1	2.3	18.8	10.1	0.8	14.1	26.6	7.1	81	274.7	33.1	78.4	39.3			
	3	V4 -	32	3.6	9.1	2.2	18.3	7.8	0.8	14.7	19.3	7.4	32.6	128.7	30.7	82.8	40.8			
	4	M5in -	22.3	3.9	11.6	3.3	24.1	3.3	0.6	20.8	19.9	8.6	48.7	206.7	32.3	72.4	37.4			
	5	M8in 68	16.6	1.8	8.8	2.5	19.8	2	0.8	13.2	20	6.5	32.4	129.7	33.4	77.4	39.1			
	6	M11in 122	16.3	2.7	13.4	4.1	16.4	5.5	0.1	21.3	23.2	10.9	37.1	229.1	38.5	62.8	33.7			
	7	BA2 mS 217	22.6	3.1	9.5	2.6	23.7	4.6	0.9	9	35.9	3.9	52.2	263.9	33.3	83.5	43.4			
	8	BA3 mS 219	20	2.8	10.4	1	24.5	4.7	0.5	23.5	48.5	10.7	54.2	211.1	32.5	84.3	46.4			
	9	BA4 mS 227	17.3	3	10.3	1.4	22.9	4.6	1.8	21.5	50.1	10.5	254.1	365.1	36	67.2	34.1			
	10	BA5 mS 238	21.1	3.9	10.7	3.6	18.5	5.3	2.2	33.8	66.1	14.2	278.4	507.7	37.3	66.7	37.5			
	11	BA6 mS 246	21.1	3.8	11.6	3.5	20.4	5	2.4	19.2	44.3	8.3	144	395.4	36.1	69.9	37.1			
	12	BA7 mS 278	18.8	4.3	11.9	2.8	23.9	6.3	1.3	13.6	63.8	7	119.1	269.9	31.9	73.9	37.3			
	13	BA8 mS 292	17.5	3.2	9.6	2.6	22.5	7.7	1.1	12.9	27.2	6	140.5	338.5	33.2	70.6	36.1			
	14	BA9 mS 296	12.6	2.5	7.1	1.9	19.6	5.7	0.9	8.7	19.8	4.3	66.9	182.3	29.1	85.8	45.3			
Digestate	1	V0 -	22.9	2	12.9	nd	nd	nd	1.1	30	31.2	19.5	83.1	236.6	27	78.4	35.4			
	2	V5 -	18.2	2.3	12.3	2.7	20.1	7.2	0.4	13.7	20.7	8.6	30.3	169.7	29.1	80.5	39			
	3	V6 -	23.8	1.7	15.3	3.7	26.7	3.5	1	24.4	31.2	10	66.8	186.5	27.8	61	32.9			
	4	V10 4	22.2	2.5	9.9	2.9	17.8	5.1	1.2	24.2	26.1	11.7	94.6	171.7	33.2	66.8	37.4	nd	nd	4.9
	5	V11 5	22.5	8.5	10.2	3	30.3	3.6	1.2	29.9	27.1	13.9	77.6	188.8	32.6	65.2	35.1	nd	nd	4.3
	6	70 70	19.7	2	8.6	4.5	24.1	9.5	2.2	24.8	28.9	10.4	55.4	272.5	28.2	66.6	37.7	6.5	0.6	2.1
	7	71 71	25.5	2.5	8.7	4	24	3.9	1.6	25.3	30.8	11.1	62.8	228.8	27.4	68.4	39.7	5.8	0.5	2.2
	8	123 123	18	2.2	12.1	4.5	19.1	4.5	0.3	16	36.3	8.5	68.1	378.8	34.7	55.6	31.4	7.2	0.5	1.4
	9	124 124	14.7	1.8	11.3	4.6	21.2	4.2	0.5	35	34	9.9	153.1	397.1	33.8	61.8	29.5	nd	nd	nd
	10	GR 1.1 220	22.4	4.2	8.4	1.3	33.2	5.2	1.6	21.8	82.4	10.8	86.7	396.7	26.2	76.6	44.7	6.3	0.4	2.6
	11	GR 1.2 221	23.7	3.2	8.2	1.3	32.4	5.6	2.1	29.1	85.5	17.3	221.6	780.2	27.7	73.6	42.6	6.2	0.6	3
	12	GR 2.1 222	18.1	2.3	7.8	1.2	38.6	5.1	0.7	24.5	44.6	11.7	97.6	272.5	27.6	76.9	41.6	5.8	0.6	3.3
	13	GR 2.2 223	20.4	2.8	8	1.1	38.9	5.2	0.4	22.8	35.9	11.1	54.9	206.5	26.7	79.7	43.3	6.8	0.5	2.6
	14	GR 3.1 224	17.7	2.6	7.7	1	32.5	3.9	0.5	41.4	61.8	11.1	77.6	215.5	27.6	78.6	42.2	5.9	0.7	3.4
	15	GR 3.2 225	20.7	3	8.1	1.1	36.5	6	0.6	25.4	40.8	8.7	80.5	264.9	26.6	76.8	43.2	5.8	0.7	4
	16	GR 5.1 247	21	3.3	8	4.4	26.2	6.3	2.6	29.1	70.4	17.7	257.8	635.5	30.5	59.8	33.5	7.2	0.4	2.7
	17	GR 5.2 248	19.9	3.5	8.3	4.4	22.7	5.8	2.6	34.2	78.3	18.7	250.9	597.7	35.6	60	32.4	6.5	0.5	2.9
	18	GR 6.1 269	20.2	3.6	9.1	4.2	21.3	6.2	2.8	30.7	65.2	14.7	200.9	479.9	29.1	60.7	32.4	7.6	0.7	1
	19	GR 6.2 270	21.1	3.8	8.6	3.6	24.4	6.8	2.4	26.8	66.1	11.3	209.9	458.8	30.4	63.7	35	7.1	0.4	1
	20	GR 7.1 293	18.4	3.9	9.2	2.9	21	7.7	1.6	18.5	48.6	8.1	166.4	361.8	30.9	69.4	35.5	5.3	0.9	5.2
	21	GR 7.2 294	26	3.9	10.5	3.8	25.1	7.6	2.4	31.6	84.7	18.6	199.3	424.8	26.2	65.8	45.6	6.9	0.5	3.5
Composted digestate	1	V13 19	21.4	4	12.6	4.6	25.8	6.4	4.7	34.8	42.1	18.7	137.2	249	43.6	50.7	28			
	2	97 97	18.5	2.3	10.2	5.2	30.7	4.1	7	44.2	57.7	21.7	75.6	305.5	41.4	56.6	28.9			
	3	153 153	19.8	5.2	13.4	5.6	26	4.7	0.5	30.5	49.6	15.3	98.8	357.3	48.3	47.1	25.2			
	4	K1 241	30.7	10.2	9.9	3.9	50.6	7.3	2.9	21.6	111.4	12	158.6	677.3	42.7	60.5	32.7			
	5	K2 243	28.3	8.2	10	4.2	53.4	5.7	1.1	20.7	91.2	10.6	89.7	353	40.6	61.5	31.6			
	6	K3 249	23.2	4	9.6	4.1	39	6	1.5	26.9	64.7	9	111.6	341.7	36.7	64.4	31.6			
	7	K4 271	22.2	4.4	9.9	5.6	29.8	6.7	3.1	34.8	72.7	15.8	478.5	596.6	45.8	40.4	25			
	8	K5 273	22.2	4.5	10.5	6	30.3	7.3	3.3	77	104.7	27.7	348.8	813.5	44.7	44.3	24			
	9	K6 275	23.5	4.2	11.3	5.6	27.9	6.9	3.6	72.3	73.2	26.1	287	567.3	46.7	48.7	26.6			
	10	K7 328	21.2	4.5	11.5	3.8	26.5	7.1	2	24.2	52.3	13	175.9	387.8	37.3	60.3	32			
Composted and sieved digestate	1	V9 -	21.5	3.7	18	5.7	45.2	8.1	1	30.2	47.2	15.8	57.6	259.6	53.1	55	31.8	nd	nd	1.2
	2	V12 18	18	2.9	13	5.2	23.4	10.2	1	42.4	45.2	21.7	107.4	250.2	45.5	41.3	23.8	7	nd	0.2
	3	98 98	20	2.7	10.7	5.4	32.5	3.5	2.6	32.1	54.1	15.3	93.2	376.6	37.7	54.3	29.2	7.2	0.4	0.9
	4	151 151	17	3.1	11.9	6.4	24	4.5	0.4	40.2	47.3	19.4	98.8	334.7	53.8	41.5	21.5	7.3	nd	0.5
	5	K1 f 242	30.8	5.5	10.4	4.3	48	7	2.4	39.7	169.9	23.1	163.7	702	42.7	61.6	33.7	7.7	0.3	0.4
	6	K2 f 244	31.1	5.3	10.4	4.4	51.5	6.4	1.2	21.5	67.1	11.5	96.6	350	38.4	62.6	33.3	7.3	0.6	0.5
	7	K3 f 250	29.6	4.5	10.5	4.6	45.6	6.9	1.6	29.8	70	9.5	119.5	393.2	36.6	60.7	34.4	7.5	0.4	0.8
	8	K4 f 272	19.8	4.3	10.8	5.6	30.1	6	3.1	36.1	74.8	15	334	574.1	46.8	42.1	21.8	7.1	0.5	1.4
	9	K5 f 274	24.8	4.5	10.8	5.7	29.5	7.3	3.3	60.6	113.8	30.3	355.5	732.5	49.7	44.2	25.8	7.2	0.5	1.4
	10	K6 f 276	23.4	4.5	10.9	5.3	30.1	6.7	3.4	55.6	80.2	13.5	297.9	548.9	47.7	48.8	25.8	7.3	0.6	1.7
	11	K7 f 325	24.3	4.3	12.5	4	27.5	9.4	2	23.6	56	13.3	593.8	411.1	38.3	57	31.6	7.8	0.4	0.8
	12	K8 f 326	17.3	3.6	10.9	4.2	28.5	6.9	2.2	24.6	63.1	12.7	204.5	468.7	38.8	57	30.4	6.9	0.7	0.8
	13	K9 f 327	15.7	2.4	9.8	3.3	26.5	6.5	1.4	17.7	35.5	9.1	110.2	270.1	38.4	74.7	39.7	7.6	0.5	2.4

Day	Cummluative MP of feedstock [Nl CH_4/kg VS]																																							
	M5in			M8in			M11in			BA2			BA3			BA4			BA5			BA6			BA7			BA8			BA9			BA10		
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	46	41	43	83	87	79	40	60	111	16	0	1	4	4	30	25	26	52	17	18	37	20	21	48	22	21	53	13	19	63	62	52	85	47	16	102	143			
2	96	93	100	112	117	104	85	111	222	39	16	16	29	30	59	53	52	106	38	37	72	50	48	105	53	53	113	47	63	135	135	123	135	101	182	213	289			
3	136	138	149	145	156	138	151	222	292	70	39	37	58	59	104	108	106	172	72	72	111	111	105	173	180	113	181	156	182	215	218	212	244	213	215	233	252	253	283	385
4	177	179	179	197	214	189	195	292	324	120	70	65	101	104	166	172	172	256	107	111	152	167	173	244	246	247	289	213	215	243	239	233	268	243	233	264	259	253	288	396
5	209	213	194	262	282	249	212	324	339	180	120	110	162	166	215	238	256	305	145	152	215	219	244	287	287	289	311	276	261	261	268	262	295	274	276	252	261	262	294	404
6	244	251	228	320	342	299	223	339	352	198	220	191	223	215	239	270	305	332	207	215	244	244	287	259	310	312	323	264	252	276	280	273	296	292	274	280	268	262	295	404
7	267	271	251	348	379	323	232	352	362	212	239	239	272	261	291	295	345	352	296	296	306	265	322	321	321	323	276	261	268	262	295	404	306	316	316	322	325	326	327	330
8	280	281	262	365	398	336	239	362	370	235	265	303	291	311	304	354	307	358	321	322	273	334	336	341	296	276	261	268	262	295	404	408	316	321	322	273	334	336	341	296
9	281	283	264	374	407	344	243	370	373	254	292	323	311	304	354	307	358	359	325	326	275	338	339	346	301	280	287	282	282	291	286	299	408	412	413	416	419	419	421	423
10	286	288	271	379	415	350	246	373	378	264	310	336	324	307	358	308	359	361	310	330	338	275	338	339	346	350	342	350	305	283	291	286	305	419	423	423	423	424	424	424
11	292	292	277	385	420	355	250	378	381	267	318	342	332	310	361	310	361	361	329	330	276	338	341	344	354	354	354	308	285	294	289	305	419	423	423	424	424	424	424	424
12	294	294	280	386	423	356	252	381	382	273	325	350	339	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	307	421	423	424	424	424	424	424	424
13	295	294	281	389	426	358	254	382	388	277	329	355	342	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
14	295	295	283	391	429	360	257	388	390	279	332	358	345	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
15	297	297	285	394	433	362	259	390	392	280	334	360	348	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
16	297	299	287	395	434	364	261	392	392	281	334	363	350	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
17	297	299	287	395	435	364	261	392	393	282	337	363	350	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
18	299	299	287	397	436	364	261	393	393	282	337	364	352	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
19	300	300	290	400	439	366	262	393	394	283	338	365	353	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
20	300	300	290	400	439	366	263	394	395	284	340	366	354	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
21	302	302	293	400	440	366	263	395	395	284	340	366	354	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
22	302	302	293	400	440	366	263	395	395	286	341	367	355	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
23	302	302	293	401	441	368	264	397	397	287	342	368	356	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
24	303	302	294	401	441	368	264	397	399	287	342	368	356	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
25	304	303	295	401	441	369	264	399	399	287	343	369	356	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
26	304	303	296	401	441	369	265	399	399	287	343	369	356	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
27	305	304	296	402	443	372	265	399	399	288	343	370	358	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424
28	305	304	297	402	443	372	265	401	401	288	343	370	358	310	361	310	361	361	332	334	278	341	344	354	354	354	354	308	285	294	289	309	423	424	424	424	424	424	424	424

pH																		
Day	BA 1		BA 2		BA 3		BA 4		BA 5		BA 6		BA 7		BA 8		BA 9	
	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2
0	7.87	7.68	7.23	7.25	7.42	7.30	7.59	7.54	7.81	7.86	7.93	8.18	7.41	7.16	7.73	7.69	nd	nd
1	7.82	7.62	nd	7.26	7.31	7.18	5.86	5.21	6.35	6.40	6.42	6.57	6.51	6.43	6.12	6.15	5.81	5.66
2	4.63	4.55	5.23	5.91	4.67	4.70	5.53	6.46	6.20	6.24	6.58	6.66	6.92	6.77	6.20	7.00	5.27	6.35
3	4.41	4.36	5.82	5.58	5.65	5.42	6.58	6.50	6.53	6.69	7.02	6.99	7.10	7.03	6.56	7.14	6.21	6.40
4	6.05	6.11	6.22	7.50	6.20	6.84	6.76	6.65	6.93	7.05	7.25	7.21	7.33	7.30	6.81	7.30	6.32	6.54
5	5.87	6.10	6.78	6.36	6.59	6.04	7.16	6.96	7.20	7.25	7.31	7.30	7.34	7.40	7.02	7.42	6.78	6.61
6	6.07	6.10	6.99	6.76	6.91	6.85	7.26	7.11	7.30	7.27	7.36	7.37	7.47	7.39	7.20	7.54	6.79	7.03
7	6.32	6.31	7.20	6.91	7.09	6.95	7.43	7.24	7.27	7.36	7.45	7.38	7.60	7.60	7.61	7.39	7.05	7.18
8	6.42	6.51	7.26	7.04	7.19	6.95	7.42	7.28	7.46	7.52	7.43	7.42	7.43	7.59	7.45	7.61	7.08	7.30
9	6.65	6.74	7.34	7.06	7.20	7.20	7.51	7.35	7.47	7.61	7.48	7.49	7.46	7.59	7.51	7.65	7.19	7.37
10	6.86	6.94	7.37	7.12	7.19	7.06	7.50	7.40	7.63	7.66	7.64	7.59	7.49	7.59	7.56	7.66	7.49	7.59
11	nd	nd	7.47	7.19	7.31	7.12	7.61	7.49	7.51	7.49	7.64	7.56	7.56	7.62	7.53	7.58	7.55	7.59
12	7.17	7.23	7.54	7.54	7.45	7.13	7.68	7.61	7.66	7.72	7.53	7.55	nd	nd	7.75	7.66	7.52	7.61
13	7.23	7.25	7.47	7.26	7.40	7.19	7.73	7.59	nd	nd	nd	nd	nd	nd	7.59	7.63	7.58	7.66
14	nd	nd	7.42	7.30	7.43	7.18	7.86	7.65	nd	nd	nd	nd	nd	nd	7.64	7.69	7.71	7.61

VOA [g/l]

Day	BA 1		BA 2		BA 3		BA 4		BA 5		BA 6		BA 7		BA 8		BA 9	
	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2
0	0.61	0.44	1.58	1.63	1.22	2.20	0.63	0.61	1.02	1.11	0.84	0.78	1.34	1.61	0.88	1.15	nd	nd
1	0.61	0.49	nd	1.88	1.88	2.22	2.98	3.62	4.78	4.03	5.74	6.04	4.30	4.16	2.97	2.70	2.33	3.21
2	2.76	1.44	3.20	2.45	5.51	6.62	4.93	5.10	4.52	4.32	5.49	5.65	3.64	3.78	4.83	3.39	3.78	4.59
3	5.42	3.07	4.54	4.61	5.08	6.22	4.66	4.58	3.61	3.16	4.20	4.81	3.10	3.26	4.09	3.19	5.35	4.75
4	5.11	4.70	3.57	4.39	4.79	3.39	3.73	3.98	3.02	2.67	2.37	2.74	2.31	2.65	4.11	2.49	4.63	4.07
5	5.25	4.74	2.96	3.32	4.07	3.68	2.68	2.81	2.64	1.97	1.95	2.25	1.89	2.24	3.88	2.22	4.07	3.46
6	3.88	3.83	2.55	2.97	3.11	2.91	1.80	2.11	1.95	1.78	1.66	1.88	2.35	1.61	3.20	1.70	3.39	2.85
7	4.55	3.83	1.81	3.09	2.30	2.42	1.60	1.60	1.76	1.76	1.48	1.82	1.36	1.30	2.45	1.39	2.89	2.39
8	3.74	3.68	1.59	2.90	2.16	1.64	1.41	1.70	1.59	1.51	1.39	1.67	1.16	1.17	2.13	1.19	2.39	1.72
9	3.23	3.11	1.44	2.48	1.82	2.02	1.44	1.52	1.54	1.42	1.21	1.46	1.10	1.08	2.05	1.15	1.98	1.57
10	3.05	2.77	1.43	2.26	1.60	1.67	1.15	1.39	1.05	1.02	1.14	1.45	1.15	0.97	1.77	0.98	1.54	1.33
11	nd	nd	1.21	2.07	1.53	1.63	1.12	1.24	1.00	1.00	1.06	1.36	1.06	0.98	1.40	0.98	1.62	1.23
12	1.89	1.94	1.19	1.89	1.50	1.61	1.08	1.54	0.85	0.92	0.96	1.23	nd	nd	1.31	0.88	1.53	1.16
13	1.58	1.63	1.15	1.83	1.45	1.64	0.96	0.97	nd	nd	nd	nd	nd	nd	1.25	0.98	1.38	1.10
14	nd	nd	1.22	2.20	1.39	1.47	0.80	0.83	nd	nd	nd	nd	nd	nd	1.11	0.82	1.48	1.33

COD [g/l]																		
Day	BA 1		BA 2		BA 3		BA 4		BA 5		BA 6		BA 7		BA 8		BA 9	
	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2	HY1	HY2
0	4.37	3.17	5.04	4.11	2.54	2.88	2.41	10.16	1.90	1.83	2.56	1.83	6.38	7.49	3.15	3.63	nd	nd
1	nd	nd	nd	6.61	2.55	2.63	16.85	15.11	14.60	13.65	16.15	13.65	13.95	15.48	15.65	13.88	20.10	21.70
2	19.32	19.42	14.35	18.74	16.94	24.72	14.17	15.65	13.15	11.72	13.80	11.72	9.45	9.91	15.18	9.45	18.78	16.88
3	19.51	20.00	14.20	11.30	19.08	22.10	11.74	11.56	10.15	8.99	8.01	8.99	8.43	9.18	12.58	8.80	13.46	11.83
4	18.00	18.00	7.25	8.80	13.20	8.70	10.58	11.57	7.32	6.19	5.12	6.19	6.60	7.47	10.65	7.60	11.06	9.70
5	18.08	18.10	9.00	8.30	9.20	7.60	6.19	6.57	5.32	4.44	3.34	4.44	5.76	6.42	9.48	5.50	9.97	9.07
6	4.71	7.35	5.00	8.10	8.20	6.50	4.79	5.93	4.45	3.82	3.20	3.82	5.61	4.61	7.74	4.37	8.77	7.93
7	10.97	12.21	4.97	5.37	7.00	6.55	3.73	4.39	3.91	3.34	3.21	3.34	5.66	4.69	6.29	3.66	7.59	6.06
8	9.81	7.05	3.48	5.63	5.90	6.00	3.32	3.91	4.02	3.39	3.14	3.39	4.26	4.04	5.42	3.69	6.28	5.13
9	5.62	6.13	3.06	5.58	3.12	3.34	3.20	3.60	3.59	2.97	2.91	2.97	4.02	3.92	4.89	3.46	5.49	4.41
10	nd	nd	2.82	5.91	4.21	4.46	2.90	2.89	2.78	2.45	2.73	2.45	3.60	3.66	4.19	3.08	4.21	3.87
11	nd	nd	2.73	4.89	3.92	4.15	2.66	3.13	2.38	2.36	2.49	2.36	3.47	3.47	4.17	2.83	4.67	3.79
12	4.46	5.50	2.57	4.58	3.61	4.40	2.29	2.63	nd	nd	2.39	nd	nd	nd	3.76	2.80	4.34	3.40
13	5.04	4.11	2.55	2.68	3.52	3.95	2.70	3.41	nd	nd	nd	nd	nd	nd	4.16	3.03	3.67	2.97
14	nd	nd	2.54	2.88	3.39	3.89	2.42	2.64	nd	nd	nd	nd	nd	nd	3.33	2.92	3.91	3.32

In dieser Reihe bereits erschienen

- Raab, T., Raab, A., Gerwin, W., Schopper, F. (Hrsg., 2013): Landschaftswandel - Landscape Change. - GeoRS Vol. 01.
- Raab, T., Hirsch, F., Raab, A., Schopper, F., Freytag, K. (Hrsg., 2013): Arbeitskreis Geoarchäologie - Jahrestagung 2013, 2. - 4.5.2013, BTU Cottbus. Tagungsband und Exkurionsführer. - GeoRS Vol. 02.
- Schneider, A. (2014): Spatial and temporal development of sediment mass balances during the initial phase of landform evolution in a small catchment. - GeoRS Vol. 03.
- Sut, M. (2014): Detection and behavior of iron-cyanide complexes in soils of a former Manufactured Gas Plant site. - GeoRS Vol. 04.
- Hirsch, F. (2016): Post-LGM-zeitliche Pedogenese und Geomorphodynamik in den spanischen Zentralpyrenäen. - GeoRS Vol. 05.
- Müller, F. (2017): Der Wandel der Kulturlandschaft im Raum Peitz infolge des mehrhundertjährigen Betriebes des dortigen Eisenhüttenwerkes (Mitte 16. bis 19. Jahrhundert). – GeoRS Vol. 06.

ISSN 2196 - 4122